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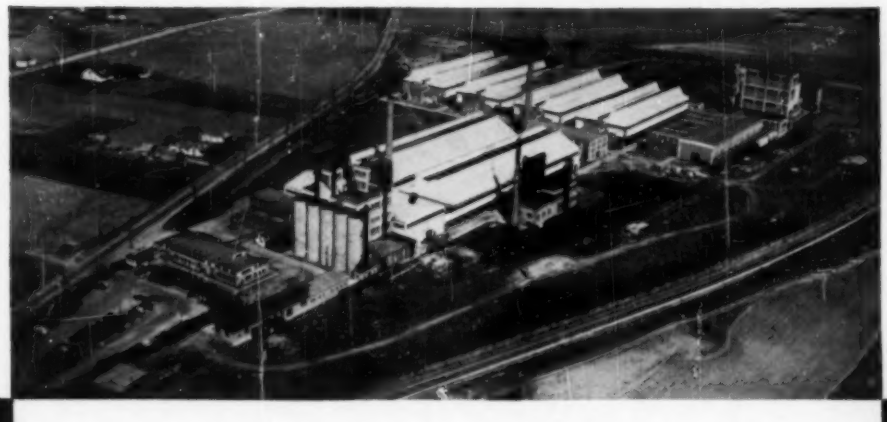

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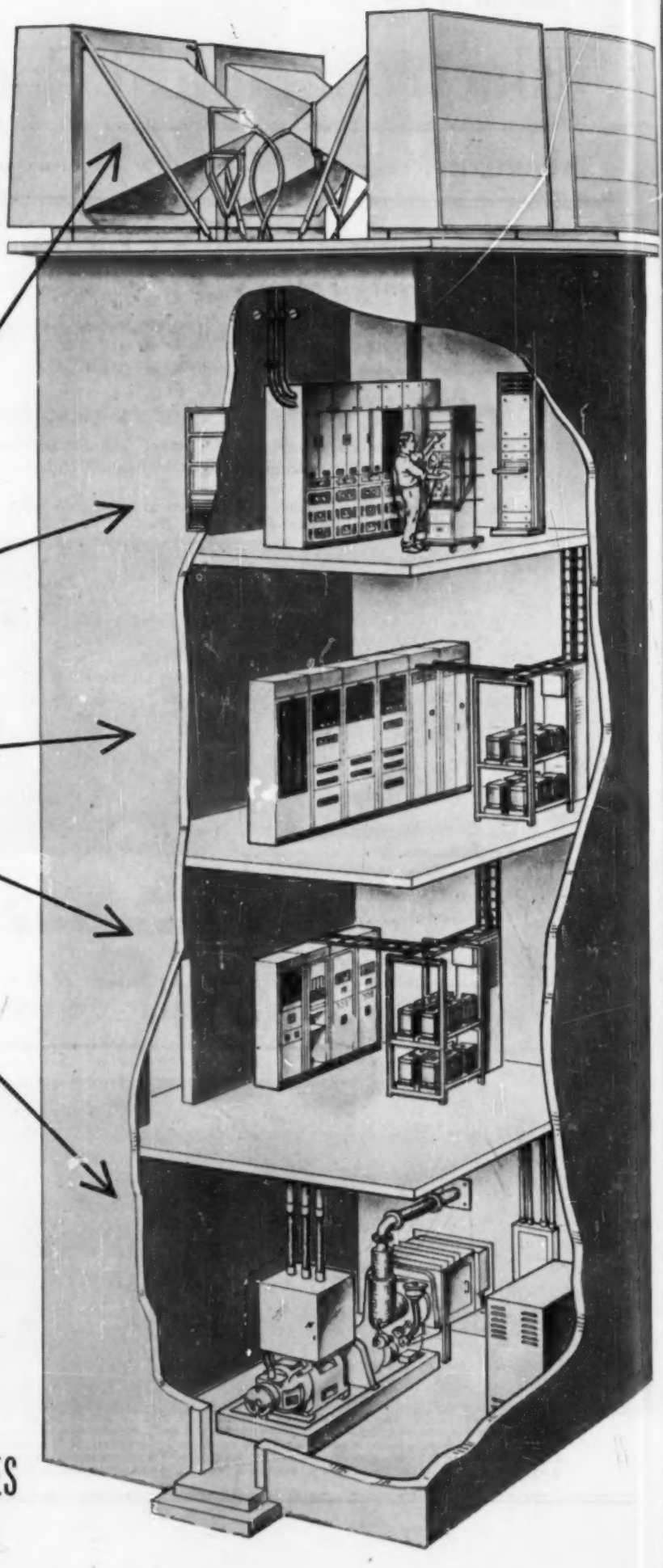

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Stress Reduction of Electrodeposited Nickel[1]

VINCENT J. MARCHESE

Sperry Gyroscope Company, Division of the Sperry Corporation, Great Neck, New York

ABSTRACT

Tests were conducted to investigate possibilities of electroforming low-stress nickel microwave plumbing. Two methods were studied: use of saccharin as an addition agent in a standard Watts bath, and superimposition of alternating current on direct current. Saccharin reduces stress in nickel deposited from the Watts bath; however, it is unstable, provides erratic results, and is difficult to control. Superimposing alternating current on direct current reduces stress considerably in nickel deposited from the Watts bath. Results verify and extend findings of previous investigations showing that stresses as low as 2,000 psi can be obtained by superimposing 60-cycle alternating current on direct current in Watts bath.

INTRODUCTION

The majority of electroforming operations for microwave plumbing involve the electrodeposition of copper. This metal has proved satisfactory in fabricating precision microwave tubing and various odd-shaped objects used in the microwave field, such as re-entrant cavities and rectangular and round adaptors. The electrodeposition of iron also is used primarily for use in wavemeter cavities because of its favorable coefficient of thermal expansion.

Nickel deposited with low internal stress offers some advantages over copper and iron because of its superior physical and corrosion-resistant properties. It has greater rigidity so that electroformed nickel microwave equipment could be made with a thinner metal wall (approximately 0.020 inch) and still be mechanically satisfactory. Also, the resultant waveguide would be almost as light in weight as one fabricated from aluminum. Electrodeposited nickel, however, as obtained from the various baths now in use, e.g., a purified Watts bath, usually has an internal tensile stress of 12,000 psi or greater. This is great enough to prevent removal of electroformed nickel from nondestructible mandrels such as steel, stainless steel, and Invar. When destructible mandrels, zinc, low melting alloys, or plastics are used, the electroformed nickel object distorts considerably upon removal of the mandrel. This is caused by internal stresses and makes it impossible to maintain close tolerances. This paper describes an electroplating system, which gives nickel deposit with low stress for application in electroforming operations.

STRESS MEASUREMENTS

Mills (1) first observed stress on plating the end of a thermometer when the mercury rose in the tube due to shrinkage of the deposit. Stoney (2) nickel-plated one side of a steel rule and noted that curvature resulted with plating on the concave side. This demonstrated the contractive stress in electrodeposited nickel and is the basis of the method which has been generally used for stress measurement.

Equipment used for the present study was a modification of that described by Phillips and Clifton (3), and Soderberg and Graham (4). It consisted essentially of a Bakelite fixture to accommodate a strip of spring steel 1.6 by 15 by 0.038 cm (0.625 by 0.015 inches) (see Fig. 1). Bakelite strips supported the steel sample rigidly on the fixture and provided shielding to give uniform current distribution. Contact to the work was made by means of a stainless steel screw extending through the metal backing plate and just touching the steel strip. Stop-off lacquer was utilized to insulate the backing plate during plating, and electroplating tape was used to cover the stainless steel screws.

In order to measure deflection of the strip after plating, the fixture shown in Fig. 1 was used. This is a modification of the holder used by Phillips and Clifton (3). In place of an indicator dial to measure curvature, a micrometer screw was used in conjunction with a one-volt lamp and battery to show when contact was made. Readings were found to be reproducible within 10 per cent. This procedure falls under Method II as classified by Brenner and Senderoff (5), hence their equation was used in calculating stress values:

$$S = \frac{E(t+d)^3}{3rd(2t+d)} = \frac{E(t+d)^3}{3d(2t+d)}\,\frac{8Z}{L^2}$$

where S is stress in the plated layer, E is the modulus of elasticity of the basic metal and nickel deposit, t is the thickness of the basic metal, d is the thickness of the coating, Z is the deflection of the strip after release, and L is the length of the test section between knife edges of the stress gage.

[1] Manuscript received July 18, 1951. This paper prepared for delivery before the Detroit Meeting, October 9 to 12, 1951.

Substituting the actual values used, there is obtained for each 0.001-inch deflection:

$$S = \frac{30 \cdot 10^6 (0.0153 + 0.0010)^3 \, 8 \cdot 10^{-3}}{3 \cdot 10^{-3} (0.0306 + 0.001) 3^2} = 1220 \text{ psi.}$$

Stress Reduction by Means of Organic Addition Agents

Organic addition agents have been used in nickel plating solution to reduce stress. Martin (6) reported that nickel formate, nickel acetate, and nickel citrate reduced stress somewhat, but not to a great extent. Hothersall (7, 8) added 5 g/l of sodium naphthalene trisulfonate to the Watts nickel bath and found the stress to be approximately zero. Saccharin (4, 9) also has been used for the same purpose. No data, however, on the stability of either saccharin or sodium naphthalene trisulfonate during plating were reported. Since past experience with sodium naphthalene trisulfonate had shown this addition agent to be uncontrollable, the first tests here were made with saccharin additions to determine their effect on stress and the extent to which the process could be controlled.

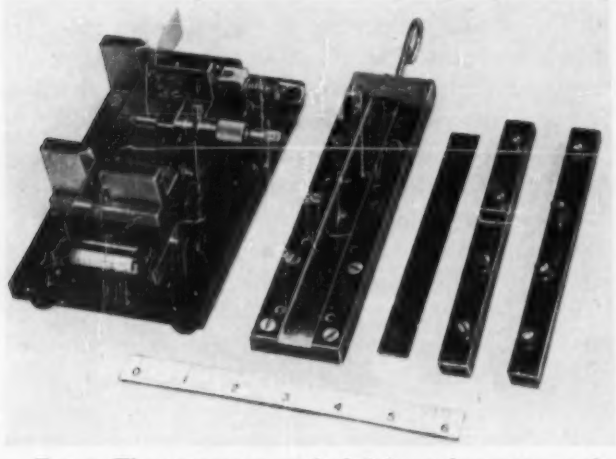

Fig. 1. The apparatus on the left is used to measure the deflection of the strip after plating. The elements on the right are the fixture in which the steel strip is supported during plating, the steel strip, and two Bakelite strips to clamp the steel to the fixture.

The standard Watts nickel bath used for all tests had the following composition:

$NiSO_4$—330 g/l (44.0 oz/gal)
$NiCl_2$—45 g/l (6.0 oz/gal)
H_3BO_3—30 g/l (4.0 oz/gal)

Purification of the bath followed the standard procedure with the bath maintained at 63° ± 0.5°C (145° ± 0.5°F) for all tests. Continuous filtration was provided by means of a specially designed all-glass reciprocating pumpand all-glass filter. Soxhlet extraction thimbles were used as the filtering medium.

An extensive number of tests were made using saccharin as the addition agent in the Watts bath. A test consisted of adding 0.1 g/l of saccharin to the bath and measuring stress after definite intervals of plating time. It was considered complete when stress had risen to a value that was considered too high to be useful for electroforming. At the end of that test an additional 0.1 g/l of saccharin was added and stress measurements were again taken after intervals of plating time in amp-hr/l. Fig. 2 presents in graphical form the data obtained during these test runs. The data show that the effects of saccharin on stress are short lived. In order to determine whether daily additions of hydrogen peroxide were causing the saccharin to decompose, a test was run without peroxide (see Fig. 3). Although the saccharin still broke down, decomposition was considerably slower; but results were so erratic that control of a plating solution to give a low stress would not bepractical Note that

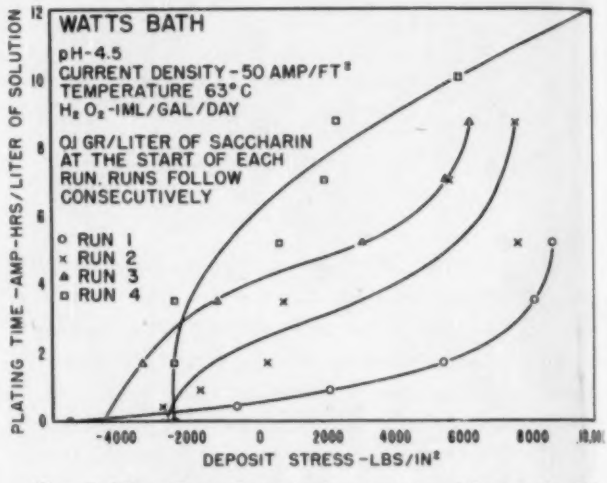

Fig. 2. The effect of saccharin on stress. After each addition of saccharin, the rate of increase of stress becomes smaller.

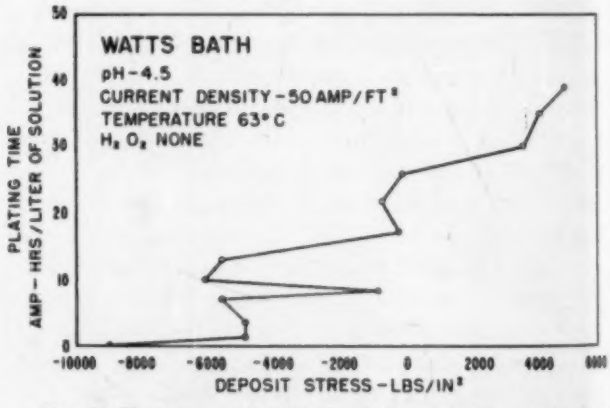

Fig. 3. Erratic results obtained when the use of hydrogen peroxide in the Watts bath was discontinued.

after each 0.1 g/l saccharin addition the stress was compressive, i.e., the test strip curved away from the nickel plate. In each case, however, after a short interval of plating time the stress soon became tensile in character.

A similar run was made except that the *p*H of the Watts bath was reduced to 2.0. In this case 0.5 g/l of saccharin was required to reduce the stress below zero. However, the stress measurements became very erratic, in fact, so much so that stress was first compressive, then went tensive, and back to compressive again for no apparent reason. On the basis of these results, further tests on organic addition agents were discontinued.

Stress Reduction by Means of Superimposing Alternating Current on Direct Current

Reduction of stress in nickel deposits by superimposing alternating current on direct current during the plating cycle has been reported (10, 11). Barklie and Davies (12) superimposed 50-cycle alternating current on direct current in such a way that nickel deposited during the cathodic pulse was partially redissolved during the anodic pulse. It was found that periodically the deposition potential was almost destroyed by the anodic pulse and that during the cathodic pulse the time was not sufficient for it to increase to any large value. At this point, a reduction in stress of approximately one third of the original value was observed. Since actual stress values obtained by superimposing alternating current on direct current are reported only to a limited extent in the literature, this method was studied further.

Apparatus

An apparatus was built in which alternating current was superimposed on direct current so that the d-c voltage and current and the negative peak voltage could be read directly when the a-c peak voltage exceeded the d-c voltage. A schematic diagram of the circuit is shown in Fig. 4.

A storage battery supplied direct current and a carbon-pile rheostat controlled the current. Both the d-c voltage and current were read as indicated in the circuit diagram. Alternating current in the circuit does not affect the indications of these meters; however, to prevent alternating current from injuring the meter movement, meters were selected having ranges approximately four or five times the actual d-c readings. The alternating current was supplied through a matching transformer having a secondary winding rated at 25 amperes. A Variac across the a-c supply controlled the a-c voltage adequately. By means of the rectifier circuit in conjunction with a d-c vacuum tube voltmeter, the negative peak of the superimposed a-c voltage across the nickel bath was readily measured.

Results

All stress tests involving the superimposition of alternating current on direct current were made on the Watts nickel bath described above. The bath was completely purified of organic and inorganic impurities at the start of the tests. Continuous filtration maintained a high state of purity within the bath.

Table I records the data obtained during the first set of results which indicate the effect of superimposing 60-cycle alternating current on direct current. For these tests additions of hydrogen peroxide of 1.0 ml/gal/day were made. It is interesting to note that the stress in the deposit is reduced to about one half when alternating current is superimposed on direct current. Only when the a-c peak voltage is equal to or greater than the applied d-c voltage, is stress reduced appreciably. A *p*H of 4.5 gave somewhat lower stress values than one of 2.0; at a *p*H 5.0 or above stress values increased sharply. This is in agreement with

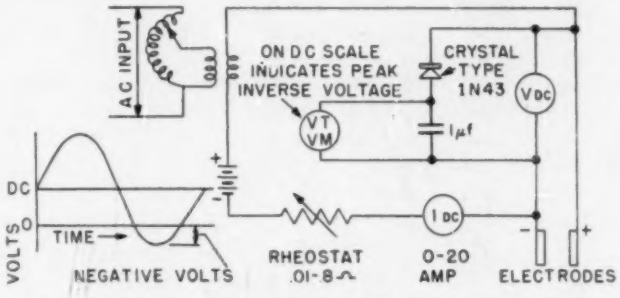

Fig. 4. Schematic diagram of circuit used to superimpose alternating current on direct current.

figures reported by Martin (6). Current density has little or no effect on internal stress of the deposit.

It became apparent early in the testing that the daily addition of hydrogen peroxide caused an increase in stress of the nickel deposit of approximately 2,500 psi. Stress did not increase immediately upon addition of the peroxide but increased gradually over a period of one hour. In the light of this phenomenon all further tests were conducted without hydrogen peroxide even though pitting of the deposit occurred. Actually, the superimposition of alternating current on direct current reduced pitting, but failed to eliminate it completely. Data showing the effect on stress of 60-cycle and 400-cycle alternating current on direct current without the addition of hydrogen peroxide are plotted in Fig. 5 and 6. In these figures deposit stress is plotted against the ratio of the peak voltage of the superimposed a-c to d-c voltage. The figures show a lower stress reduction of 60-cycle alternating current at both *p*H 2.0 and 4.5 than does 400-cycle alternating current. The curves indicate a minimum value of stress at both *p*H values. At a *p*H of 2.0, minimum stress is obtained at a ratio of 6.0 of a-c peak voltage to d-c voltage; at *p*H 4.5 the ratio is approximately 3.0.

TABLE I. *Stress data—superimposing alternating current on direct current—Watts bath 60-cycle alternating current*

Sample No.	Current density amp/ft²	Thickness of plate inches	Amperes dc	Amperes ac	Volts dc	Negative volts ac	Voltage ratio ac/dc	Deflection of panel inches	Stress psi	Remarks
12	50	0.0013	1.0	0.0	1.6	0.0	0.0	0.0107	13,700	*p*H 2.0, 145°F, addition of H_2O_2 1 cm³/gal/day
13	50	0.0010	1.0	0.66	1.6	0.0	0.9	0.0100	12,200	"
14	50	0.0009	1.0	1.08	1.55	0.50	1.3	0.0073	8,800	"
15	50	0.0008	1.0	1.43	1.50	1.26	1.9	0.0070	8,400	"
16	50	0.0010	1.0	2.43	1.50	2.60	2.7	0.0060	7,300	"
17	50	0.0090	1.0	3.36	1.45	4.07	3.8	0.0038	4,600	"
18	50	0.0090	1.0	3.36	1.45	4.07	3.8	0.0059	7,100	"
19	25	0.0010	0.5	3.5	0.8	4.7	6.9	0.0058	7,100	"
21	20	0.0010	0.42	1.07	0.8	1.2	2.5	0.0055	6,700	"
22	40	0.0010	0.85	1.8	1.3	2.0	2.5	0.0058	7,100	"
23	80	0.0010	1.65	3.0	2.1	3.3	2.5	0.0050	6,100	"
24	50	0.0011	1.0	0.0	2.2	0.0	0.0	0.0223	27,700	*p*H 5.0, 145°F, addition of H_2O_2 1 cm³/gal/day
25	50	0.0011	1.0	0.0	2.2	0.0	0.0	0.0196	24,300	"
26	50	0.0010	1.0	0.0	2.2	0.0	0.0	0.0108	13,200	*p*H 4.5, 145°F, addition of H_2O_2 1 cm³/gal/day
28	50	0.0010	1.0	0.66	1.7	0.7	0.8	0.0123	15,000	"
29	50	0.0010	1.0	1.1	1.8	0.3	1.2	0.0073	8,900	"
30	50	0.0010	1.0	1.4	1.8	1.0	1.0	0.0051	6,200	"
31	50	0.0010	1.0	2.4	1.6	2.5	2.6	0.0050	6,100	"
32	50	0.0008	1.0	3.3	1.7	3.7	3.3	0.0059	7,000	"
33	20	0.0010	0.4	1.0	0.8	1.0	2.3	0.0050	6,100	"
34	40	0.0010	0.9	1.8	1.3	1.8	2.4	0.0040	4,900	"
35	80	0.0010	1.7	3.4	2.2	3.3	2.5	0.0046	5,600	"
1J	50	0.0008			1.5	0.0	1.0	0.0088	10,400	*p*H 2.5, no H_2O_2
2J	50	0.0010			1.5	1.0	1.7	0.0043	5,200	"
3J	50	0.0010			1.4	2.0	2.4	0.0054	6,600	"
4J	50	0.0010			1.3	3.0	3.3	0.0034	4,200	"
5J	50	0.0010			1.3	4.0	4.1	0.0029	3,500	"
6J	50	0.0010			1.3	6.0	5.6	0.0039	4,800	"
7J	50	0.0010			1.3	8.0	7.2	0.0033	4,000	"
8J	50	0.0010			1.2	10.0	9.3	0.0037	4,500	"

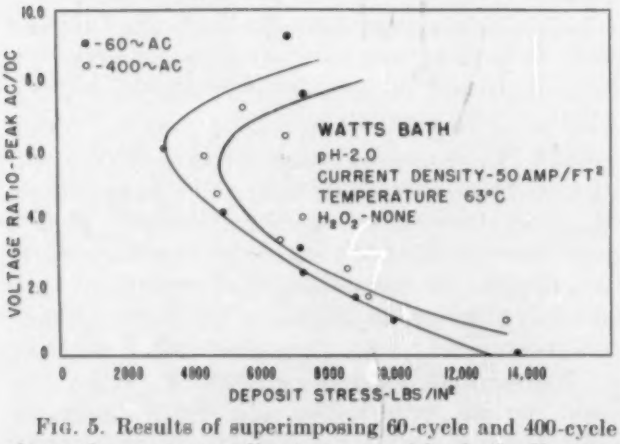

FIG. 5. Results of superimposing 60-cycle and 400-cycle alternating current on direct current with a bath *p*H of 4.5.

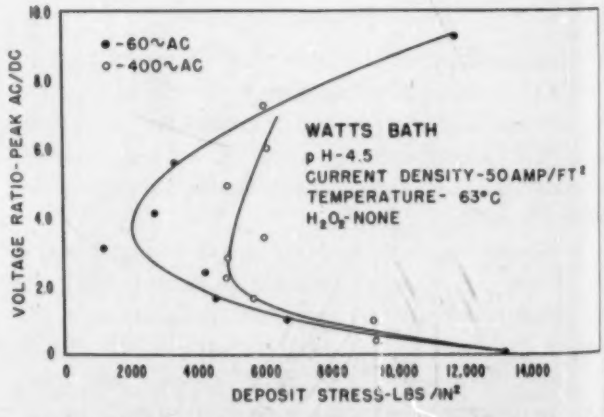

FIG. 6. Results of superimposing 60-cycle and 400-cycle alternating current on direct current with a bath *p*H of 2.0.

Electroforming Tests

For electroforming purposes, the plating conditions which produced minimum stress were used, i.e., a *p*H of 4.5 and 60-cycle alternating current superimposed on direct current in a peak voltage ratio of three to one. To eliminate pitting, 0.1 g/l of Duponol M.E. Dry wetting agent was added. Addition of this wetting agent not only eliminated pitting but also appeared to eliminate striations within the deposit. The effect of Duponol M.E. Dry on the stress within the deposit was checked and it was found that no apparent change could be measured

at a bath *p*H of 4.5, the same curve as shown in Fig. 6 was obtained.

Actual electroforming on Invar mandrels was conducted as follows. A nonadherent silver layer approximately 0.0001 inch thick was plated on the Invar mandrel followed by approximately 0.0002 inch of nickel from a cold Watts bath to avoid any lifting of the nonadherent silver layer. Electroforming was then continued in the heated Watts bath using the plating conditions described above. This produced an electroformed waveguide containing a silver layer on the internal surface for conduction purposes. To date, a number of waveguides approximately $\frac{1}{4}$-inch long, and some wavemeter cavities approximately $\frac{3}{4}$ inch in diameter, have been made. In all cases, no difficulty has been experienced in removing the electroformed nickel from the Invar mandrel, indicating that the internal stress within the deposit is apparently low even in heavy sections.

It was noticed that wherever heavy deposits of nickel were plated under the condition of minimum stress as defined above, the buildup at edges and sharp corners was not similar to the nodular deposit usually obtained with the conventional Watts bath. Some treeing of the deposit was noticed that resembled the type of structure obtained with the iron bath. This could be eliminated by the use of thieves at the high current density edges or by the use of shields. For this work, thieves were used satisfactorily.

Acutal experience with nickel electroforming by means of superimposing alternating current on direct current has been very limited. Indications are that the process is a feasible one, however, and parts can be electroformed with a low internal stress so that distortion can be held to a minimum.

Conclusions

1. Stress within the nickel deposit could be made compressive by adding saccharin in excess of the amount required to reduce the stress to zero.

2. The use of saccharin as an addition agent to reduce internal stress in nickel deposited from a Watts bath gave erratic results, and control of such a solution would not be practical.

3. Superimposing alternating current on direct current reduced stress in nickel deposited from the Watts bath.

4. Minimum stress of approximately 2,500 psi was obtained when 60-cycle alternating current was superimposed on direct current at a ratio of a-c peak voltage to d-c voltage of three to one and at a bath *p*H of 4.5.

5. Hydrogen peroxide increased stress in the Watts bath and should not be used. Duponol M.E. Dry is a satisfactory wetting agent to use to reduce pitting of the deposit.

Acknowledgment

The author wishes to express his appreciation of the efforts of Mr. J. S. Russo, also of the Sperry Gyroscope Company, who conducted some of the laboratory work which provided the basis for this paper.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1952 issue of the Journal.

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Electrodeposition of Rhenium-Cobalt and Rhenium-Iron Alloys[1]

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ABSTRACT

Electrodeposition of rhenium-cobalt and rhenium-iron alloys from an aqueous ammoniacal citrate solution is described. The effects of bath composition, *p*H, temperature, and current density on cathode current efficiency and composition of the alloy deposit were studied. A rhenium-cobalt solution, containing 60 g/l of $CoSO_4 \cdot 7H_2O$, 10 g/l of $KReO_4$, 66 g/l of citric acid, and NH_4OH to *p*H 7, when electrolyzed at 5 amp/dm² and 70°C gave a cathode deposit containing 75 per cent rhenium with a current efficiency of about 85 per cent. A rhenium-iron solution, containing 59.4 g/l of $FeSO_4 \cdot 7H_2O$, 10 g/l of $KReO_4$, 66 g/l of citric acid, and NH_4OH to *p*H 7, when electrolyzed at the same conditions gave a cathode deposit containing 85 per cent rhenium with a current efficiency of 65 per cent.

Introduction

In a recent article describing the electrodeposition of rhenium-nickel alloys from an ammoniacal citrate plating bath (1), it was mentioned that rhenium-cobalt and rhenium-iron alloys could be electrodeposited from the same type of plating solution. The electrodeposition of rhenium-cobalt has been previously noted (2), although not described in detail, but apparently there is no previous mention of the electrodeposition of rhenium-iron alloys.

The present work was undertaken for the purpose of determining suitable conditions for the electrodeposition of rhenium-cobalt and rhenium-iron alloys from an ammoniacal citrate plating bath. The effects of bath composition and electrolysis conditions on cathode current efficiency and on the composition of the alloy deposit were of special interest. A Hull cell was used to obtain qualitative information about the performance of the plating solutions but all results reported here were obtained by regular electrolysis methods. No attempt was made to find uses for these electrodeposited rhenium alloys; however, some of their properties were examined briefly.

Experimental Procedure

The experimental methods were the same as described for the electrodeposition of rhenium-nickel alloys (1), except for a few necessary changes. Iron anodes were used with the rhenium-iron bath and either platinum or cobalt electrodeposited on platinum was used as anode material in the rhenium-cobalt plating solution. Electrodeposited alloys to be analyzed were dissolved from the insoluble platinum cathode by sulfuric acid and hydrogen peroxide and the alloying metal was separated from rhenium with sodium hydroxide solution. Quantitative analysis methods used were: rhenium gravimetrically as nitron perrhenate; cobalt electrolytically; and iron volumetrically by the Zimmermann-Reinhardt method.

Current efficiency calculations were based on the original oxidation states of the bath components—cobalt (II), iron (II), and rhenium (VII). No doubt both iron and cobalt are partially oxidized, to M (III), in the plating solutions; however, since the extent of their oxidation in these solutions is not known, the original oxidation states were used in the calculations.

Experimental Results

Rhenium-Cobalt

The rhenium-cobalt bath contained 60 g/l of $CoSO_4 \cdot 7H_2O$, 10 g/l of $KReO_4$, and 66 g/l of citric acid. Ammonium hydroxide was added to the solution to give the *p*H desired.

Bath pH.—In this study the temperature of the plating bath was maintained at 70°C and a current density of 5 amp/dm² was used. The *p*H of the solution was varied from 3 to 8 and the effect of *p*H changes was observed by noting the cathode current efficiency and the rhenium content of the alloy deposit obtained at each *p*H. The results, given in Fig. 1, show that the percentage of rhenium in the cathode deposit is lowest, 65 per cent, at *p*H 4 and highest, 82 per cent, at *p*H 8. Cathode current efficiency is best, about 90 per cent, at *p*H 5 and then decreases somewhat as the *p*H is increased. The same series of experiments was repeated at a cathode

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current density of 10 amp/dm² instead of 5 amp/dm²; the effect was the same as shown in Fig. 1 except that at each *p*H both current efficiency and rhenium

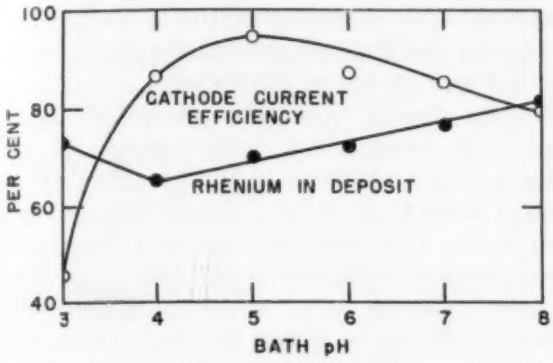

FIG. 1. The effect of bath *p*H on the rhenium-cobalt bath. Bath contains 60 g/l of $CoSO_4 \cdot 7H_2O$, 10 g/l of $KReO_4$, and 66 g/l of citric acid. Temperature 70°C; cathode current density 5 amp/dm².

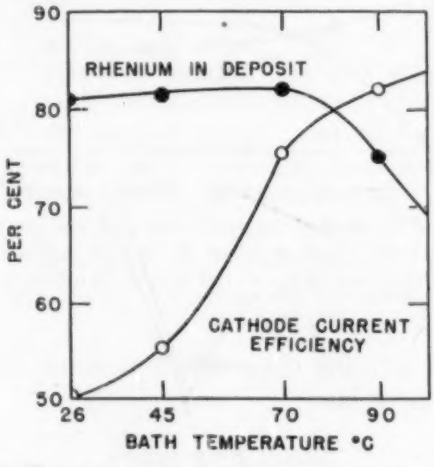

FIG. 2. The effect of bath temperature on the rhenium-cobalt bath. Bath contains 60 g/l of $CoSO_4 \cdot 7H_2O$, 10 g/l of $KReO_4$, and 66 g/l of citric acid. Cathode current density 8 amp/dm²; *p*H 7.6.

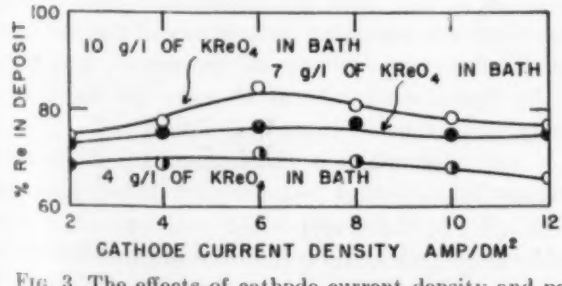

FIG. 3. The effects of cathode current density and perrhenate concentration on the percentage of rhenium in the cathode deposits from the rhenium-cobalt bath. Bath contains 60 g/l of $CoSO_4 \cdot 7H_2O$, $KReO_4$ as indicated, and 66 g/l of citric acid. Temperature 70°C; *p*H 7.6.

content of the deposit were slightly lower. These results, together with Hull cell observations, indicate that a rhenium-cobalt bath having a *p*H of 7 to 8 should give satisfactory performance.

Bath temperature.—For this study bath temperatures of 26°, 45°, 70°, and 90° ± 2°C were used and in each case the cathode current density was 8 amp/dm² and bath *p*H was 7.6. The results given in Fig. 2 show that temperature has a marked effect on cathode current efficiency and only a slight effect on the rhenium content of the alloy deposit. It was concluded that a bath temperature of about 70°C would be used for additional work.

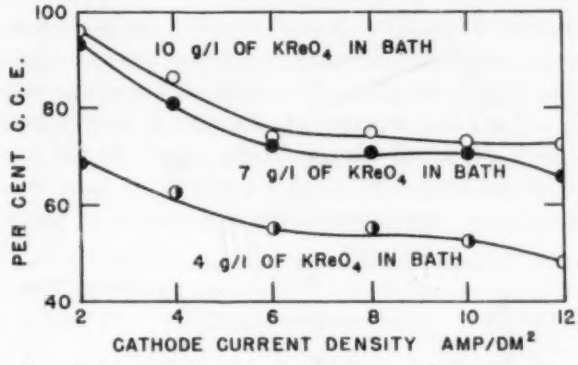

FIG. 4. The effects of cathode current density and perrhenate concentration on the cathode current efficiency of the rhenium-cobalt bath. Bath contains 60 g/l of $CoSO_4 \cdot 7H_2O$, $KReO_4$ as indicated, and 66 g/l of citric acid. Temperature 70°C; *p*H 7.6.

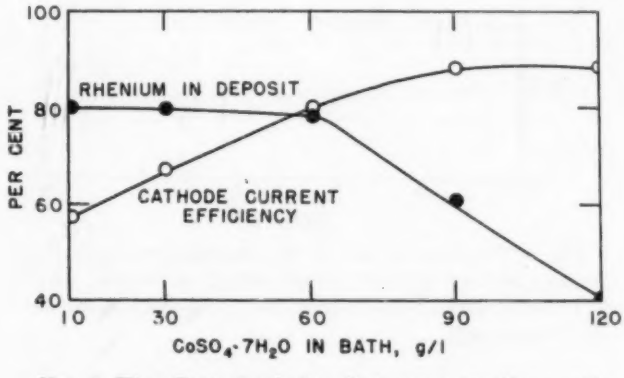

FIG. 5. The effect of cobalt sulfate concentration on the rhenium-cobalt bath. Bath contains cobalt sulfate as indicated, 10 g/l of $KReO_4$, and 66 g/l of citric acid. Temperature 70°C; *p*H 8; cathode current density 5 amp/dm².

Current density; potassium perrhenate concentration.—The effect of cathode current density was determined using the regular rhenium-cobalt bath (10 g/l of $KReO_4$) and also baths containing 7 and 4 g/l of $KReO_4$. In each case bath *p*H was 7.6 and temperature was 70°C. The results given in Fig. 3 show that current density has very little effect on the percentage of rhenium in the deposit and that increasing the concentration of rhenium in the bath increases the amount of rhenium in the alloy deposit somewhat. Fig. 4 shows that current efficiency decreases somewhat, at all three concentrations of potassium perrhenate, as the current density is increased.

Cobalt sulfate concentration.—For this determination the amount of cobalt sulfate in the plating solution was varied from 10 to 120 g/l while the concentration of the other components was the same as in the regular rhenium-cobalt bath. Bath temperature was maintained at 70°C, *p*H was 8, and a cathode current density of 5 amp/dm² was used. Fig. 5 shows that current efficiency increases from about 60 per cent to 90 per cent as the cobalt sulfate concentration is increased from 10 to 120 g/l. The composition of the alloy deposit remains fairly constant as the cobalt sulfate concentration is increased from 10 to 60 g/l, but when the cobalt sulfate is increased to 120 g/l the amount of rhenium in the cathode deposit drops off sharply from about 80 per cent to 40 per cent. The same general effect was noted when these experiments were repeated at a current

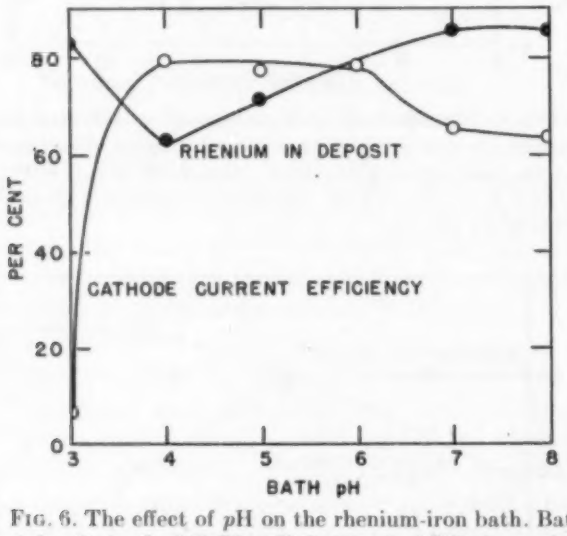

FIG. 6. The effect of *p*H on the rhenium-iron bath. Bath contains 59.4 g/l of $FeSO_4 \cdot 7H_2O$, 10 g/l of $KReO_4$, and 66 g/l of citric acid. Temperature 70°C; cathode current density 5 amp/dm².

density of 10 amp/dm² instead of 5 amp/dm²; however, the rhenium content of the deposits and the current efficiencies were slightly lower at the higher current density.

Rhenium-Iron

The rhenium-iron bath contained 59.4 g/l of $FeSO_4 \cdot 7H_2O$, 10 g/l of $KReO_4$, and 66 g/l of citric acid. Ammonium hydroxide was added to the solution to give the *p*H desired.

Bath pH.—For this study a temperature of 70°C was maintained, cathode current density was 5 amp/dm², and *p*H was varied from 3 to 8. As can be seen in Fig. 6 current efficiency rises sharply as the *p*H is changed from 3 to 4 and then decreases somewhat as the *p*H is increased to 8. The rhenium content of the alloy deposit reaches a minimum at *p*H 4 and then increases gradually to about 85 per cent at *p*H 8. The same general effect of *p*H was noted when a current density of 10 amp/dm² was used instead of 5 amp/dm²; however, current efficiencies and the rhenium content of the alloys were somewhat lower at this higher current density. These results and the Hull cell results indicate that a bath *p*H of 6 to 8 should be satisfactory.

Current density.—The effect of cathode current density on rhenium-iron deposition was observed using a bath temperature of 70°C, a *p*H of 7.6, and current densities from 2 to 12 amp/dm². As can be seen in Fig. 7 the rhenium content of the alloy deposit decreases somewhat as the current density is increased, whereas current efficiency increases up to a current density of 6 amp/dm² and then remains fairly constant. The same general trend was observed using baths containing less potassium perrhenate

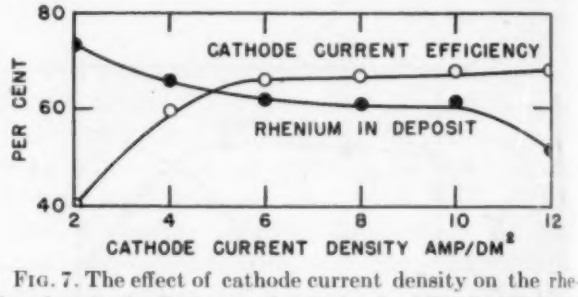

FIG. 7. The effect of cathode current density on the rhenium-iron bath. Bath contains 59.4 g/l of $FeSO_4 \cdot 7H_2O$, 10 g/l of $KReO_4$, and 66 g/l of citric acid. Temperature 70°C; *p*H 7.6.

(4 and 7 g/l), but the results were rather erratic so are not given here.

ALLOY PROPERTIES

Electrodeposited rhenium-iron alloys were generally brighter than rhenium-cobalt or rhenium-nickel alloys, although some of the iron alloys obtained at low bath *p*H values and high current densities were somewhat dull. Many of the rhenium-cobalt alloys were silvery in appearance and some of the deposits obtained at 10 amp/dm² had a tendency to peel away from the basis metal.

It was observed that rhenium-cobalt alloys were perhaps less resistant to laboratory fumes than the other alloys. Electrodeposited rhenium-nickel and rhenium-iron remained bright and untarnished when exposed to laboratory air for three months whereas rhenium-cobalt became somewhat dull and gray. Electrodeposited rhenium under similar conditions became quite dark in ten days, and in three months the entire plate was covered with a dark nonadherent corrosion product; when this was rubbed off a bright surface of rhenium was again visible. The resistance of electrodeposited rhenium-nickel to common reagents (1) was perhaps somewhat better than was

observed for rhenium-cobalt and rhenium-iron, although there were no very marked differences. In all these cases the alloy was plated on copper.

Discussion

A comparison of the characteristics of the rhenium-cobalt, rhenium-iron, and rhenium-nickel (1) plating solutions shows that, in general, rhenium-cobalt and rhenium-iron solutions are quite similar to each other and that both are quite different from rhenium-nickel solutions. For example, whereas *p*H variations of the rhenium-nickel bath have only a minor effect on the rhenium content of the alloy deposits (Ref. 1, Fig. 2), *p*H variations of the other solutions have a fairly marked influence on the composition of the electrodeposited alloy. It is to be noted also that both rhenium-cobalt and rhenium-iron plating solutions give alloy deposits with a minimum rhenium content at a bath *p*H of 4.

The mechanism of the cathode process involved in the electrodeposition of these rhenium alloys is somewhat uncertain but the assumed presence of certain types of coordination complexes can be used to explain the high rhenium content of the alloys. The formula for one of the cobalt ammine complex rhenium salts that has been prepared (3) is $Co(NH_3)_6(ReO_4)_3$. According to Werner's theory of coordination compounds this type of compound may undergo isomerism in solution to give the following types of ions:

$$[Co(NH_3)_5ReO_4]^{++} \text{ and } [Co(NH_3)_4(ReO_4)_2]^{+}.$$

If it can be assumed that similar nickel, and perhaps iron (II), complexes are also formed, then the plating solutions will all contain rhenium in a positively charged complex ion. Such a positive ion would be transported to the cathode more readily than a negative ion which would approach the cathode by diffusion. Thus, the rather high rhenium content of the alloy deposits and the fairly high current efficiencies are explainable. It is quite probable that the presence of citrate ion in the plating solutions affects the types of complex ions present and thus adds to the complexity of the reduction process.

It is felt that the mechanism of the electrodeposition of these alloys of rhenium with iron, nickel, and cobalt will not be understood until the electrodeposition of the single metals (Ni, Co, or Fe) from citrate solutions has been studied thoroughly.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1952 issue of the Journal.

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The Electrodeposition of Cobalt-Tungsten-Molybdenum Alloys from Aqueous Citrate Solutions[1]

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ABSTRACT

The electrodeposition of cobalt-tungsten-molybdenum alloys is described. The aqueous plating bath was prepared from sodium tungstate, sodium molybdate, cobalt sulfate, and citric acid. The *p*H of the solution was adjusted by the addition of either ammonium hydroxide or dilute sulfuric acid. A Hull cell and regular plating procedures were used to determine optimum bath concentrations and electrolysis conditions. It was found that a bath containing 0.23 mole per liter of cobalt sulfate, a total of 0.23 mole per liter of sodium tungstate and sodium molybdate (W:Mo mole ratio of 7:3), and 0.31 mole per liter of citric acid gave satisfactory performance. When this plating solution was adjusted to *p*H 4 and maintained at 25°C, electrolysis at 5 amp/dm² gave a cathode deposit containing 66 per cent cobalt, 21 per cent molybdenum, and 13 per cent tungsten with a cathode current efficiency of 73 per cent.

Introduction

The electroreduction of aqueous tungstate or molybdate solutions in the presence of nickel, cobalt, or iron salts to give various binary alloys as cathode deposits has been reported a number of times (1–5), but there has been very little interest in the electrodeposition of ternary alloys from similar solutions. The electrodeposition of nickel-cobalt-tungsten alloys from an acid plating solution has been reported (6) and electroplated ternary alloys containing nickel, cobalt, and tungsten and also iron, cobalt, and tungsten have been described briefly (5). Recently, in reporting the electrodeposition of molybdenum alloys (4), it was noted that ternary alloys containing tungsten, molybdenum, and a codepositing metal could be electroplated from similar solutions. In the present work the electrodeposition of cobalt-tungsten-molybdenum alloys from a citrate type of aqueous plating solution was investigated. The work was limited to citrate solutions because this type of bath was used to obtain most of the binary tungsten or molybdenum alloys previously reported. Since neither tungsten nor molybdenum has been electroplated alone in appreciable amounts from aqueous solution, it was felt that electrodeposited ternary alloys containing these two metals and a codepositing metal would be of some interest. Cobalt was selected as the codepositing metal for this study although it is probable that either iron or nickel would have served equally well. The main purpose of the investigation was to gain more information about the electroreduction of aqueous tungstate and molybdate solutions.

Experimental

All the plating solutions used in this study were prepared from sodium molybdate, sodium tungstate dihydrate, cobalt sulfate heptahydrate, and citric acid monohydrate. In preparing the baths, the desired amounts of cobalt sulfate and citric acid were first dissolved in water and then the sodium molybdate and sodium tungstate were added. The *p*H of the solution was adjusted by the addition of ammonium hydroxide or dilute (1:5) sulfuric acid. All *p*H determinations were made with a glass electrode.

The experimental work was organized to bring out the effects of such factors as bath composition, bath *p*H, and bath temperature on cathode current efficiency and on the appearance and composition of the cathode deposits. Preliminary qualitative information was obtained with the Hull cell but all quantitative information was of necessity obtained by using regular plating procedures.

Hull Cell Results

The design and operation of the Hull cell has been described by the inventor (7). The 267-ml model used in this work was equipped with a 6.4 cm x 10.2 cm copper cathode and a 6.4 cm x 6.4 cm platinum anode. A current of 3 amperes, supplied by a variable voltage rectifier, was used; this current gave a cathode current density range of from about 1 amp/dm² to 16 amp/dm². External cooling was necessary when the solutions were used at room temperature even though the period of electrolysis was only five minutes. The appearance of the Hull cell

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cathodes was used as a measure of the effect of various changes in bath composition over a *p*H range of from 2 to 10. About fifty Hull cell runs were made to obtain the qualitative information described below.

Sodium molybdate concentration.—The solutions used for this study contained 60 g/l of $CoSO_4 \cdot 7H_2O$, 40 g/l of $Na_2WO_4 \cdot 2H_2O$, 66 g/l of citric acid, and variable amounts (2, 10, 20, 30, or 40 g/l) of Na_2MoO_4. Each bath with a given concentration of sodium molybdate was used at *p*H values of 2, 4, 6, 8, and 10. Temperature was maintained at 25°C except in a few cases where the temperature was 70°C. The resulting Hull cell cathodes indicated that: a bath *p*H of 4 is best for all the concentrations of sodium molybdate used; baths with lower concentrations of sodium molybdate (2 and 10 g/l) have the greatest current density range of deposition; a bath temperature of 25°C is much better than a bath temperature of 70°C.

Sodium tungstate concentration.—The solutions used for this work contained 60 g/l of $CoSO_4 \cdot 7H_2O$, 10 g/l of Na_2MoO_4, 66 g/l of citric acid, and variable amounts (2, 20, or 40 g/l) of $Na_2WO_4 \cdot 2H_2O$. Each bath with a given concentration of sodium tungstate was used at *p*H values of 2, 4, 6, 8, and 10. The resulting Hull cell cathodes indicated that: a bath *p*H of 4 is best; varying the concentration of sodium tungstate seems to have no significant effect on the current density range of deposition.

Cobalt sulfate concentration.—The solutions used for this purpose contained 40 g/l of $Na_2WO_4 \cdot 2H_2O$, 10 g/l of Na_2MoO_4, 66 g/l of citric acid, and variable amounts (2, 20, 60, or 80 g/l) of $CoSO_4 \cdot 7H_2O$. Each bath with a given concentration of cobalt sulfate was used at *p*H values of 2, 4, 6, 8, and 10. The resulting Hull cell cathodes indicated that: a bath *p*H of 4 is best; increased cobalt sulfate concentration gives increased current density range of deposition; at 80 g/l of cobalt sulfate and bath *p*H 10 there is a new bright plating range.

Bath concentration in moles/liter.—It is obvious that the composition of the cathode deposit is dependent on the actual as well as the relative concentration of the plating solution. To make comparative values more significant the concentration of each bath ingredient was expressed in terms of moles per liter instead of grams per liter. To study this concentration effect, baths were made up containing fixed amounts of cobalt sulfate and citric acid and variable amounts of total tungstate + molybdate but with a 1:1 mole ratio of tungstate to molybdate. The baths were made up to contain 0.23 mole (64.5 g) per liter of $CoSO_4 \cdot 7H_2O$, 0.31 mole (66 g) per liter of citric acid, and decreasing amounts of total tungstate + molybdate (1:1 mole ratio) from 0.46 mole (76 g/l $Na_2WO_4 \cdot 2H_2O$ + 47.5 g/l Na_2MoO_4) to 0.057 mole/liter. The bath *p*H was 4 and the temperature was 25°C in each case. The resulting Hull cell plates (Fig. 1) show that as the concentration of tungstate + molybdate in the bath decreased, the appearance of the plates became progressively better until a concentration of 0.057 mole/liter gave a mirror bright surface over the whole Hull cell cathode.

Quantitative Results

Regular plating procedures were used to obtain quantitative information about the electrodeposition of these alloys. The electrolytic cells, 250-ml beakers, containing 225 ml of plating solution, were placed in a water thermostat to maintain a bath temperature of about 25°C. Each cell was equipped with two

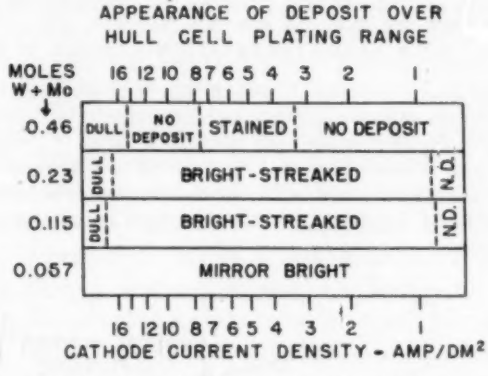

Fig. 1. Hull cell cathodes showing the plating range of solutions containing varying amounts of total sodium tungstate + sodium molybdate. Baths contain (per liter): 0.23 mole of cobalt sulfate, 0.31 mole of citric acid, and the indicated amount of tungstate + molybdate in a 1:1 mole ratio. Bath *p*H 4; temperature 25°C; total current 3 amperes; time 5 minutes. (Current density values are approximations.)

platinum anodes and a gold cathode, all 3 cm x 3 cm in size. Usually several electrolytic cells were operated in series with a copper coulometer.

The analysis of these alloys was complicated by the difficulty of making a complete separation of tungsten and molybdenum. Since the presence of an organic reagent such as cinchonine is known to give high values for the tungsten in the presence of molybdenum, due to coprecipitation of molybdenum, it was decided to precipitate tungstic acid without the addition of cinchonine even though this results in slightly low values for tungsten. After removal of the precipitated tungstic acid, the cobalt was separated with sodium hydroxide and then determined electrolytically using a Slomin electroanalyzer. Molybdenum was determined gravimetrically by precipitation as lead molybdate. The use of an insoluble gold cathode simplified the analysis somewhat. In some

cases the amount of molybdenum was estimated by difference after the percentages of cobalt and tungsten in the alloy deposit had been determined.

Cathode current efficiency calculations were based upon the analysis of the cathode deposit, the necessary chemical equivalents, and the weight of copper deposited on the copper coulometer cathode.

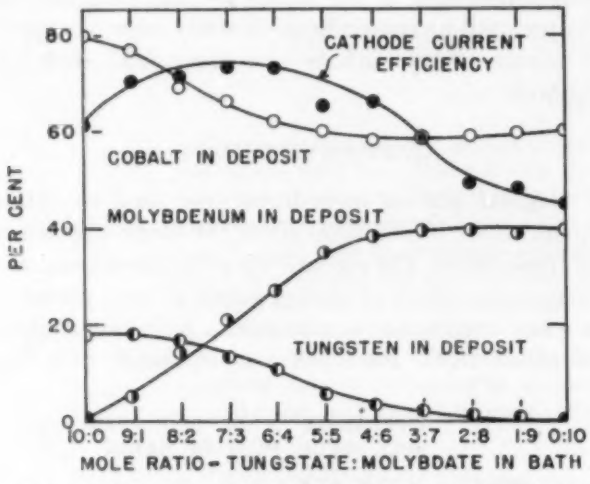

FIG. 2. The effect of the tungstate-molybdate mole ratio on cathode current efficiency and composition of the cathode deposit. Baths contain (per liter): 0.23 mole of cobalt sulfate, 0.31 mole of citric acid, and a total of 0.23 mole of sodium tungstate + sodium molybdate in the ratios indicated. Bath *p*H 4; temperature 25°C; cathode current density 5 amp/dm².

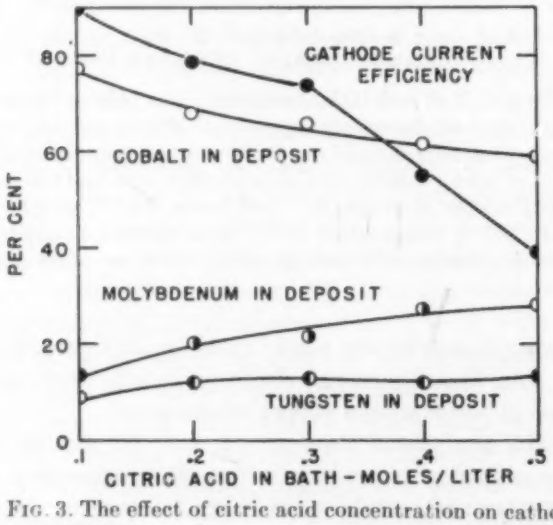

FIG. 3. The effect of citric acid concentration on cathode current efficiency and composition of the cathode deposit. Baths contain (per liter): 0.23 mole of cobalt sulfate, 0.23 mole of sodium tungstate + sodium molybdate (7:3 mole ratio), and citric acid. Bath *p*H 4; temperature 25°C; cathode current density 5 amp/dm².

Mole ratio of tungstate to molybdate.—The Hull cell results (Fig. 1) showed that the total combined concentration of tungstate and molybdate should be less than 0.46 mole/liter, so a concentration of 0.23 mole/liter was used for additional work; however, there was no reason to suppose that the 1:1 mole ratio of tungstate to molybdate gave the best deposits, so the effect of changing this ratio was studied.

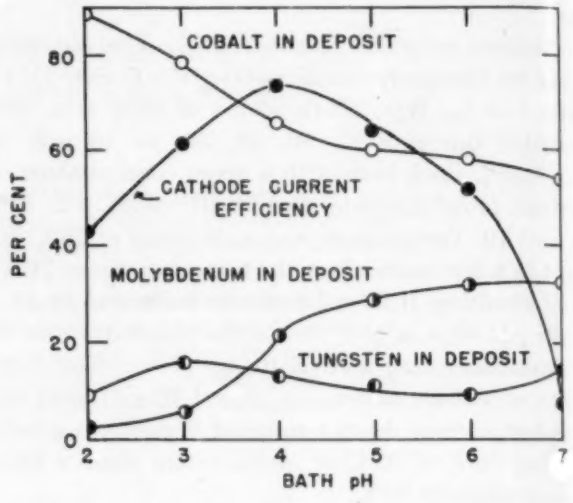

FIG. 4. The effect of bath *p*H on cathode current efficiency and composition of the cathode deposit. Baths contain (per liter): 0.23 mole of cobalt sulfate, 0.23 mole of sodium tungstate + sodium molybdate (7:3 mole ratio), and 0.31 mole of citric acid. Cathode current density 5 amp/dm²; temperature 25°C.

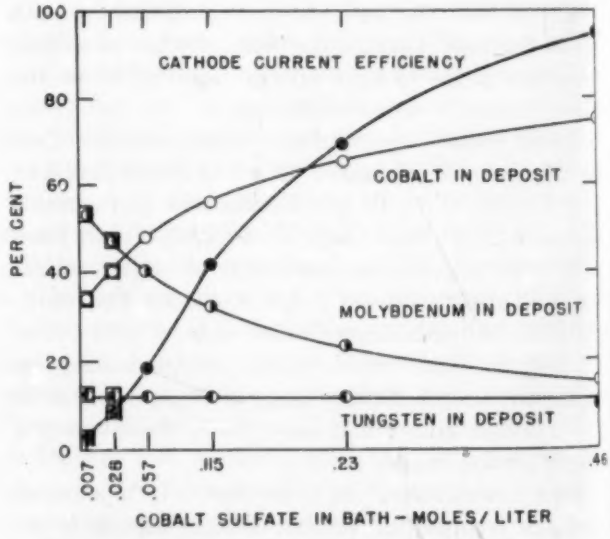

FIG. 5. The effect of cobalt sulfate concentration on cathode current efficiency and composition of the cathode deposit. Baths contain (per liter): 0.23 mole of sodium tungstate + sodium molybdate (7:3 mole ratio), 0.31 mole of citric acid, and cobalt sulfate. Bath *p*H 4; temperature 25°C; cathode current density 5 amp/dm² except that 15 amp/dm² were used at the two lowest concentrations of cobalt sulfate. Points on the graph which are enclosed in squares are the values obtained at 15 amp/dm².

A number of baths were prepared with 0.23 mole/liter of cobalt sulfate, 0.31 mole/liter of citric acid, and with a total of 0.23 mole/liter of sodium tungstate + sodium molybdate in varying mole ratios.

The ratio of tungstate to molybdate was varied from 10:0 (0.23 mole of tungstate, no molybdate) to 0:10 (no tungstate, 0.23 mole of molybdate). The baths were adjusted to *p*H 4 and maintained at 25°C during electrolysis at 5 amp/dm². Fig. 2 shows the cathode current efficiencies and the analyses of the cathode deposits obtained from these baths. It can be concluded from these results that the effect of the concentration of molybdate in the bath is much more pronounced than that of the tungstate. The amount of tungsten or molybdenum in the cathode deposit is not a linear function of the concentration in the bath; nor is the combined percentage of tungsten + molybdenum in the deposit constant. The highest current efficiency was observed in baths having W:Mo mole ratios of 7:3 and 6:4. The best appearing deposits were obtained from baths having mole ratios of from 8:2 to 5:5. At the high tungsten end of the series the deposits tended to flake off the cathode and at the high molybdenum end of the series the deposits became streaked and discolored. On the basis of these results the 7:3 mole ratio of tungstate to molybdate was selected to be used for additional work; this was prepared from 0.161 mole (53.1 g) $Na_2WO_4 \cdot 2H_2O$, and 0.069 mole (14.2 g) Na_2MoO_4, to give a total of 0.23 mole/liter of tungstate + molybdate.

Citric acid concentration.—Citric acid is a necessary component of the plating solutions and functions as a complexing agent. The effect of citric acid concentration was studied using baths containing 0.23 mole/liter of cobalt sulfate, 0.23 mole/liter of sodium tungstate + sodium molybdate (7:3 mole ratio), and with the concentration of citric acid varying from 0.1 to 0.5 mole/liter. Bath *p*H was 4, bath temperature 25°C, and the average cathode current density was 5 amp/dm². Fig. 3 shows the resulting current efficiencies and the composition of the cathode deposits; most noticeable is the drop in current efficiency as the citric acid concentration was increased from 0.3 to 0.5 mole/liter.

Bath pH.—Solutions containing 0.23 mole/liter of cobalt sulfate, 0.23 mole/liter of sodium tungstate + sodium molybdate (7:3 mole ratio), and 0.31 mole/liter of citric acid were used in this study. Bath *p*H was varied from 2 to 7, temperature was 25°C and cathode current density was 5 amp/dm². Fig. 4 shows the resulting current efficiencies and the composition of the cathode deposits. It is to be noted that as the *p*H increased, the amount of tungsten in the deposit remained fairly constant, whereas the amount of molybdenum increased and the amount of cobalt decreased. Maximum current efficiency was at *p*H 4 and the best appearing deposits were obtained in the *p*H range 3 to 6. These results confirmed the previously described Hull cell results which indicated that a bath *p*H of 4 was perhaps the most satisfactory.

Cobalt sulfate concentration.—Solutions containing 0.23 mole/liter of tungstate + molybdate (7:3 mole ratio), 0.31 mole/liter of citric acid, and varying amounts of cobalt sulfate (from 0.007 to 0.46 mole/liter) were used. Bath *p*H was 4, temperature was 25°C, and the average cathode current density was 5 amp/dm² except that 15 amp/dm² were required in order to get a cathode deposit at the two lowest concentrations of cobalt sulfate. Fig. 5 shows the resulting current efficiencies and the composition of the cathode deposits. It is to be noted that, as the cobalt sulfate concentration increased, the percentage of tungsten in the deposit was unchanged, the percentage of molybdenum decreased, the percentage of cobalt increased, and the cathode current efficiency increased.

Anodes.—Platinum anodes were used in all the work that has been described. In some brief exploratory work it was found that cobalt and molybdenum were satisfactory as anodes; however, tungsten seemed unsatisfactory as it became highly polarized and the flow of current dropped off rapidly.

Alloy properties.—No attempt was made to study the properties of these electrodeposited Co-W-Mo alloys. However, a cursory examination of the alloy deposited on a low carbon steel rod indicated that the plate was rather soft. It could be scratched easily with a file and seemed softer than electrodeposited binary alloys of tungsten.

Other ternary alloys.—Additional work has shown that the following ternary alloys can be electrodeposited from the citrate type of plating solution: Fe-W-Mo, Ni-W-Mo, Co-Ni-W, Fe-Co-W, Fe-Ni-W, Co-Ni-Mo, Fe-Co-Mo, Fe-Ni-Mo, and Fe-Co-Ni.

Discussion

An examination of the experimental results makes it evident that tungstates and molybdates behave quite differently in these plating solutions. For example, when the concentration of citric acid in the bath was increased, the amount of tungsten in the cathode deposit changed very little whereas the amount of molybdenum increased very markedly (Fig. 3). When the concentration of cobalt sulfate in the bath was increased there was no marked change in the tungsten content of the cathode deposits while the molybdenum content decreased considerably (Fig. 5). When the bath *p*H was increased the amount of tungsten in the deposit did not change appreciably while the molybdenum increased considerably (Fig. 4). These differences are somewhat unexpected and difficult to explain when one considers the chemical similarity of tungsten and molybdenum.

No attempt was made to identify the various ions and complexes which are present in the plating solutions, but some reasonable guesses as to their identity can be made. Cobalt is probably present as a citrate complex and (or) as an ammine. The *p*H of the solution would be expected to have an effect on the oxidation state of the cobalt and the type of complex which predominates. It is quite likely, particularly with solutions containing excess ammonia, that cobalt (III) ammines would predominate since under these conditions the trivalent state of cobalt is the more stable; however, the effect of the citrate ion and citrate complexes on these ammines is not known. The normal tungstates and molybdates added to the plating solutions would perhaps remain as such only in basic solutions. Various polytungstates and polymolybdates are known to form when the normal salts are carefully acidified, and no doubt compounds of this type are present in some of the plating solutions. The fact that poly-acids of molybdenum are more numerous than are those of tungsten may help to explain some of the differences in behavior of tungstates and molybdates which have already been noted. Some of the known derivatives of molybdic acid and tungstic acid with citric acid could also be present in the plating solutions. This lack of definite information about the substances present in the baths makes it impossible to suggest at this time a reasonable mechanism for the process whereby aqueous tungstates and molybdates are electrolytically reduced in the presence of cobalt compounds.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1952 issue of the JOURNAL.

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Electroforming Aluminum Waveguides Using Organo-Aluminum Plating Baths[1]

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ABSTRACT

Aluminum waveguides with twists, bends, and/or tapers were electroformed by electrodepositing aluminum on electropolished, copper-plated, cadmium-nickel-alloy mandrels, followed by melting out the cadmium-nickel alloy and dissolving out the copper in nitric acid solution. This is a new procedure for obtaining mirrorlike inner surfaces of electroformed articles. The aluminum walls (0.65 to 1.0 mm thick) were dense, strong, and ductile. The high-purity aluminum electrodeposits were as hard as 138 Knoop. The plating baths consisted of a dispersion of toluene in a toluene solution of the fusion product of ethyl pyridinium bromide and aluminum chloride with methyl *t*-butyl ether or another addition agent for improving the physical properties of the aluminum electrodeposits[2]. The baths were used for as long as 560 amp-hr/l (44 days) and could have been used longer if necessary.

Introduction

The electrodeposition of aluminum was investigated with the objective of making light-weight waveguides that could be tested for radar wave-transmission characteristics. A wall thickness of at least 0.5 mm was required for rigidity and strength. A satisfactory process was developed for electrodepositing aluminum 0.65 mm or more thick. Suitable deposits of aluminum exceeding 0.05 mm in thickness were not obtainable by any method tested according to reports in the literature. In the preliminary tests, the bath described by Hurley and Wier (1–3) produced better aluminum plate than any of the others. It was prepared by fusing one mole of ethyl pyridinium bromide with two moles of anhydrous aluminum chloride and adding benzene or toluene until a second layer formed on top of the plating solution. Aluminum was plated on cathodes in the lower layer.

Attempts to electrodeposit aluminum thicker than 0.05 mm (0.002 in.) resulted in "lacey" nodular metal unsuitable for waveguide surfaces. The bath needed some kind of modification if electroforms were to be achieved with the required wall thickness. When a good plate was produced, by improvements described herein, the more commonly used low-melting alloys for mandrels were found unsuitable for "clean" removal from the aluminum electroforms.

Experimental

Preliminary Results

The ethyl pyridinium bromide-aluminum chloride fusion product dissolved in toluene was greatly improved[3] through the use of an organic addition agent and by dispersion of toluene in the solution of the fusion product and addition agent. A new improved electrical system was also devised.

The plating baths were made up by the following formula:

Constituent	Per cent by weight
Fusion product of 1 mole of ethyl pyridinium bromide + 2 moles of aluminum chloride	32
Toluene (sp gr 0.866)	67
Methyl *t*-butyl ether	1

An extensive series of preliminary experiments led to the selection of the methyl *t*-butyl ether as the best addition agent effecting the necessary improvement in the aluminum plate. Other addition agents effecting smooth and dense plates are reported in a following section.

The specific resistivity of the lower layer [solution of fusion product (eutectic) in toluene without dispersed excess toluene] was 6.8 ohm-cm at 30°C (85°F). The methyl *t*-butyl ether is soluble in the lower layer. The upper layer of toluene was nonconducting and could be dispersed by gas (nitrogen) agitation in the lower layer. When the gas agitation was stopped, the bath again separated into two layers, which were easily redispersed for plating. Then, with the gas agitation and the methyl *t*-butyl ether addition agent, sound, dense, aluminum plate was made in thicknesses up to 1 mm (0.040 in.).

The fusion product of ethyl pyridinium bromide and aluminum chloride was prepared by slowly adding molten ethyl pyridinium bromide (mp 114°–116°C) from a dropping funnel to anhydrous alumi-

[1] Manuscript received October 15, 1951. This paper prepared for delivery before the Montreal Meeting, October 27 to 31, 1952.

[2] Subject of a patent application.

[3] Subject of a patent application.

num chloride protected against air with nitrogen or argon gas. The reaction was completed by heating the mixture at 200°C for 15 minutes. Two moles, or 58.7 parts by weight, of aluminum chloride and one mole, or 41.3 parts by weight, of ethyl pyridinium bromide form a eutectic that melts at about −40°C. The composition of representative batches of the fusion product deviated slightly from the theoretical composition of the eutectic. The bromine and chlorine contents of the products were less than the calculated bromine and chlorine contents of the eutectic. The aluminum content was slightly greater than the calculated aluminum content of the eutectic. Hydrogen halide was evolved when ethyl pyridinium bromide was fused with aluminum chloride.

To account for the loss in hydrogen halide and the gain in aluminum, at least one complex, besides

TABLE I. *Composition of ethyl pyridinium bromide-aluminum chloride fusion products*

Constituent	Theoretical composition of $C_5H_5N(Br)C_2H_5 \cdot Al_2Cl_6$	Per cent found, by weight
Aluminum	11.9	11.9 to 12.5, by analysis
Chlorine	47.0	45.7 to 46.7, by analysis
Bromine	17.6	15.8 to 17.2, by analysis
$C_5H_5N(Br)C_2H_5 \cdot Al_2Cl_6$	100	4.3 to 63.5, calculated
$[C_5H_4N(Br)C_2H_5 \cdot Al_2Cl_6]_3 \cdot Al$	—	34.9 to 88.2, calculated
Free HCl	—	0.3 to 4.1, calculated

the eutectic, must be assumed. The complex $[C_5H_4N(Br)C_2H_5 \cdot Al_2Cl_6]_3 \cdot Al$ is a possibility. The weight fractions of the eutectic, of $[C_5H_4N(Br)C_2H_5 \cdot Al_2Cl_6]_3 \cdot Al$, and of free HCl were calculated on the basis of the aluminum, chlorine, and bromine contents. The results of the calculations are given in Table I. Fusion products in the composition range shown in Table I produced equally good deposits of aluminum when dissolved in toluene, and agitated to disperse the excess toluene, and when an addition agent was used.

Ethyl pyridinium bromide was prepared by mixing equimolecular proportions of pyridine and ethyl bromide with nitrogen gas passing over the mixture to protect it from oxidation and hydrolysis. The temperature of the reaction was kept below 35°C by running cold water over the reaction flask. Crystals of ethyl pyridinium bromide began to form after 15 to 30 minutes. After 48 hours, the product was recrystallized three times in xylene. Xylene was removed by vacuum distillation, starting at 25°C and heating to 150°C in about 30 minutes. The yield was 85 per cent, or more. The melting point of the product was 114° to 116°C.

Electroforming Cell and Operating Conditions

During the preliminary studies to establish suitable addition agents and conditions for electrodepositing sound, thick aluminum plate, 250-ml baths were used. Ultimately, 9-liter baths were used for producing segments of waveguides for tests to measure the transmission efficacy of aluminum electroforms with mirrorlike interior surfaces.

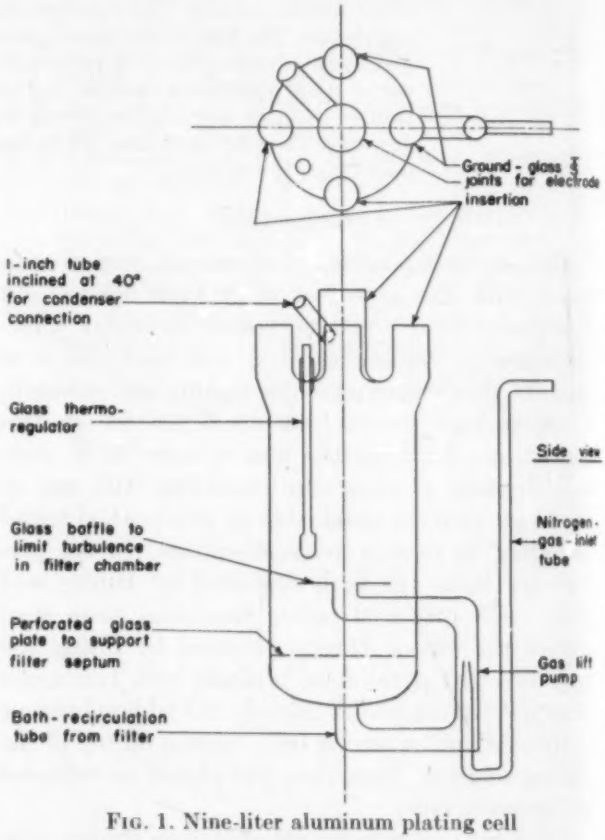
Ground-glass joints for electrode insertion
1-inch tube inclined at 40° for condenser connection
Glass thermo-regulator
Side view
Nitrogen-gas-inlet tube
Glass baffle to limit turbulence in filter chamber
Perforated glass plate to support filter septum
Gas lift pump
Bath-recirculation tube from filter

FIG. 1. Nine-liter aluminum plating cell

The 9-liter bath was contained in the Pyrex glass plating cell shown in Fig. 1. The electrodes were suspended from tapered 28 aluminum plugs fitting the tapered glass joints at the top of the cell. The mandrel (cathode) was suspended in the center of the cell and four aluminum anodes (assaying 99.9 per cent aluminum) were placed around the side of the cell. A water-cooled condenser was fitted into the inclined tube at the top. Thus, continuously condensed toluene was returned to the plating bath. The plating solution was continuously filtered while it was pumped with the gas-lift pump from the bottom of the cell and returned to the cell at a higher level. The filter bed, supported by the perforated glass plate, was composed of glass wool. The plating temperature was maintained at 30° ± 1°C with a

375-watt infrared heating bulb focused on one side of the cell and controlled with a thermoregulator.

Tank nitrogen gas passed through a tube packed with copper turnings and heated to 650°C to remove oxygen. It was then bubbled through toluene to compensate for the toluene carried out of the plating bath with the exit gas stream. The volume of excess toluene in the bath was adjusted by regulating the temperature of the toluene in the bubble tower and the flow of cold water to the condenser, which was the gas outlet. The rate of the gas flow was regulated by a tank valve and was measured with a manometer. It was maintained at the rate predetermined to be about 50 per cent more than that needed to disperse

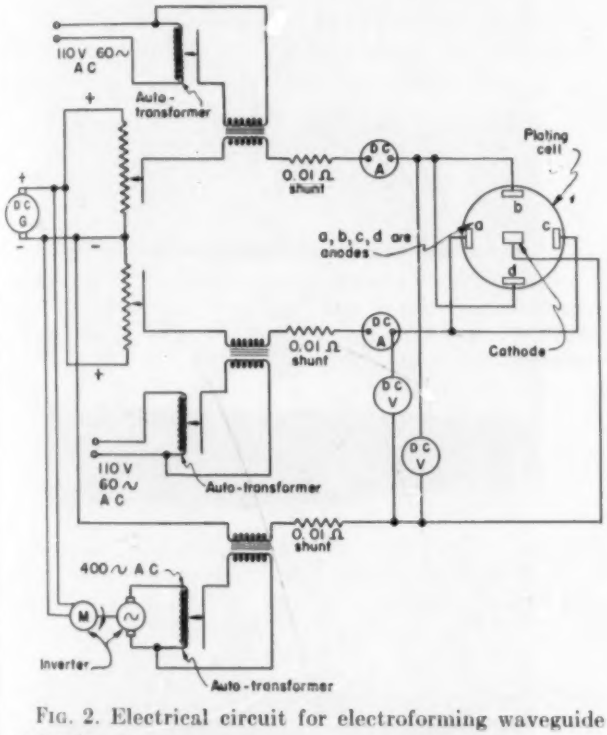

FIG. 2. Electrical circuit for electroforming waveguide segments.

the excess toluene in the solution of fusion product in toluene, about 0.2 m³/hr.

The electrical equipment included a 6-volt d-c generator, a transformer for 60-cycle a-c, an autotransformer for 60-cycle a-c, a generator for 400-cycle a-c, an autotransformer for 400-cycle a-c, and a rheostat for d-c. Shunts were placed in the circuit so that a vacuum-tube voltmeter could be used to measure a-c in amperes. The electrical circuit is shown in Fig. 2.

The a-c density on the anodes and cathode was regulated independently by adjusting the 60-cycle a-c superimposed between the anodes or the 400-cycle a-c superimposed on the d-c. The d-c density on the cathode was 1.1 to 2.2 amp/dm² (10 to 20 amp/ft²). With no a-c superimposed on the d-c, the aluminum electrodeposits were highly stressed and were sometimes cracked. Excessive a-c superimposed on the d-c caused the electrodeposits to become nodular.

The cathode current efficiency, based on d-c only, was generally 91 to 95 per cent. The d-c voltage between the cathode and the anodes was between 1.5 and 2.0 volts. The a-c voltage between the cathode and the anodes was between 1.5 and 2.5 volts.

The d-c density on the anodes was 1.5 to 3 amp/dm² (14 and 28 amp/ft²). The a-c density on the anodes was 1.1 to 1.3 amp/dm² (10 to 12 amp/ft²). A lower a-c density on the anodes caused an anode sludge (principally silicon-containing phase) to dislodge, resulting in nodular plate. The anode current efficiency, based on d-c only, was between 101 and 105 per cent. Hydrogen halide was continuously evolved from the bath at the rate of 0.01 g/hr, or less. It evidently reacted with the aluminum electrodes, causing the anode efficiency to be slightly greater than 100 per cent, and the cathode efficiency to be slightly less than 100 per cent.

The Mandrels

The mandrels were cast to the proper outside dimensions to provide the exact inside dimensions of the waveguide, the inside surface of which thus became the mirror image of the outside surface of the mandrel. Cadmium-nickel alloy (containing 1 to 2% nickel) provided better castings than alloys of lead with antimony, bismuth, or other metals to give very low melting points.

To cast the mandrels, the cadmium-nickel alloy was superheated to about 480°C and was poured in a graphite-coated steel mold preheated to 430°C. The mold was chilled on the outside with cold water, freezing the melt progressively from the bottom to the top. The complex-shaped mandrels were machined from large slabs of the alloy to avoid the cost of making special molds.

After grinding the surfaces, the castings were plated with about 0.07 mm of copper (approximately 0.003 in.) in a copper pyrophosphate bath (4) at 52°C with a cathode current density of about 2 amp/dm² (18.6 amp/ft²). Smooth, mirrorlike surfaces were produced by electropolishing the copper-plated mandrels in a chromic acid-phosphoric acid bath (5).

After electrodepositing 0.65 to 1.0 mm (0.025 to 0.040 in.) aluminum on the mandrels, the ends of the segments were trimmed to the desired length [generally 17.7 cm (7 in.)] and the alloy was melted out by heating to 370°C. The copper plate and the small particles of the alloy that adhered to the copper were dissolved in a nitric acid solution (sp gr 1.42), which was maintained at 40°C (104°F) or less to avoid etching the aluminum. After rinsing, the wave-

guides were dipped in a cleaning solution composed of 85 per cent phosphoric acid (by weight), saturated with chromic acid at 70°C, and, finally, rinsed and dried.

Without the copper plate, particles of the mandrel, after melting out, clung to the surface of the aluminum electroform and were difficult to remove without damaging the aluminum surface. Neither did the cadmium-nickel alloy melt out clean from the copper. However, the copper was easily dissolved away in nitric acid, leaving a mirror-finished aluminum surface.

FIG. 3. Experimental aluminum waveguide segments. *Left to right:* flanged straight segment; tapered segment; and segment with a 90° bend and a 90° twist.

Appearance, Purity, and Properties of the Electroformed Waveguides

Examination of the inner surfaces of the waveguides with a boroscope, which magnified the image 10 diameters, showed no surface irregularities. Most of the waveguides produced by the procedure described in the preceding sections had good ductility and strength.

The methyl *t*-butyl ether or another addition agent was necessary in the original bath formulation to cause the outer surfaces of the 0.65- to 1.0-mm thick (0.025 to 0.040 in.) electrodeposits to be smooth. When the smoothening agent was omitted, deposits exceeding about 0.2 mm (0.008 in.) in thickness were nodular. The nodular deposits were not so hard as the smooth plates. The microhardness of the cross sections was between 28 and 36 Knoop for the nodular plate and between 36 and 138 Knoop for the smooth deposits.

Representative waveguides made during this investigation are shown in Fig. 3. The outer surfaces of these waveguide segments are the same as they were when removed from the bath. The ends were cut off to prescribed lengths.

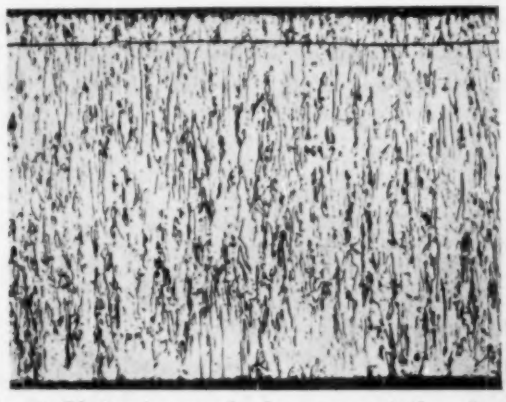

FIG. 4. Photomicrograph of a representative aluminum electroform produced with the proper operating conditions. Etched with 0.5 per cent HF solution. 85×. [Dense metal, essentially pore free (0.022 in. thick)].

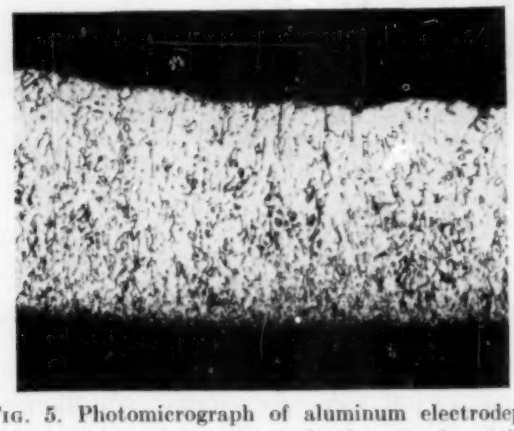

FIG. 5. Photomicrograph of aluminum electrodeposit produced with a deficient a-c density on the cathode. Etched with 0.5 per cent HF solution. 93×.

Flanges were attached by aluminum brazing after melting out the cadmium-nickel-alloy mandrel.

The ductility of aluminum plates electrodeposited during the first 24 or 48 hours after formulating a new bath was inferior to the ductility of electrodeposits produced after a 48-hour "break-in" period, which probably served to remove metallic impurities. The impurities found in a plate electrodeposited after a 24-hour "break-in" period were, according to spectrographic analysis, as follows: 0.05 to 0.1 per cent silicon, 0.05 to 0.1 per cent iron, 0.01 to 0.1 per cent lead, 0.005 to 0.05 per cent copper, 0.005 to 0.05 per

cent magnesium, and less than 0.005 per cent chromium. Although the total percentage of impurities in the electrodeposit was very small, it was larger than the total percentage of impurities in the anodes. The aluminum chloride used to make the fusion product contained more metallic impurities than the other materials used in formulating the bath.

In contrast to the good ductility obtained when excess toluene was dispersed in the solution of the fusion product, only brittle electrodeposits, probably containing occluded organic matter, were obtained when the plating bath was unagitated. The addition of methyl *t*-butyl ether or another smoothening agent did not affect the ductility of the deposits made in the agitated baths.

The organic-impurity content of aluminum electrodeposits was estimated by measuring the volume of nitrogen and carbon dioxide evolved by thermal de-

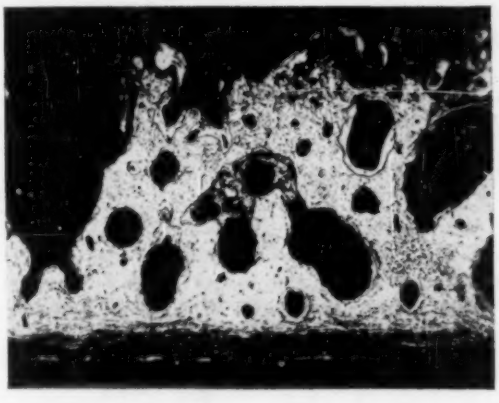

FIG. 6. Photomicrograph of an aluminum deposit produced without bath agitation. Keller's etch. 143×. [*Top:* treelike sponge metal. *Bottom:* relatively dense initial layer, not pore free (0.0015 in. thick)].

composition at 636°C. The carbon dioxide content was less than 0.005 per cent by weight, and the nitrogen content was consistently 0.01 per cent by weight. The hydrogen content of deposits produced with methyl *t*-butyl ether added to the bath for its smoothening effect was between 0.015 and 0.025 per cent by weight. The hydrogen content of a deposit produced without smoothening agent was 0.005 per cent.

Microstructure of Aluminum Electrodeposits

The microstructure of a representative aluminum electrodeposit produced with the optimum conditions described previously is shown in Fig. 4. The addition of methyl *t*-butyl ether or other agent added for smoothening purposes did not significantly affect the microstructure of the deposits. However, such addition agents caused a notable increase in the degree of orientation of the crystal planes, according to X-ray patterns. The crystal planes were highly oriented with (110) or (100) planes parallel to the basis metal. The crystals within the deposits produced without addition agents were randomly or lowly oriented.

Reducing the plating temperature (from 30° to 0°C) or reducing the a-c density on the cathode [from 1.1 to less than 0.5 amp/dm^2 (10 to < 5 amp/ft^2)] caused grain refinement and high stress in the plate, as are illustrated in Fig. 5. Cracking resulted when the stress was excessive.

For comparison purposes, the structure of a deposit produced without bath agitation to produce good toluene dispersion is shown in Fig. 6.

Addition Agents

Nine addition agents, besides methyl *t*-butyl ether, caused an improvement in the outer surface smoothness of thick aluminum electrodeposits. In general, aromatic ethers were equally as effective as the alkyl ethers. Besides the ethers, certain substituted phenyl amines and chlorinated alkyl hydrocarbons were effective. Alkyl aldehydes were very good smoothening agents, but caused such a high stress that the deposits were cracked. The most effective hardeners were methyl *t*-butyl ether and dimethylaniline.

Discussion of the Results

A few years ago, aluminum electroplates 0.05 mm (0.002 in.) thick were considered to be the maximum obtainable. Thicker deposits became powdery and spongy. Thick electrodeposits with improved physical properties can be obtained now by a method believed to have opened the door for commercial applications of electrodepositing aluminum.

Aluminum waveguides were made for the first time by the procedure described herein. Other procedures may be developed in the near future, now that such an accomplishment has been shown to be technically possible. The results of this investigation are believed to be sufficiently encouraging for ultimate large-scale use of aluminum electrodeposition.

Further investigation is recommended on the electrodeposition of aluminum as a protective coating against corrosion. Commercial-grade chemicals have been used to secure good electrodeposits, but more information is needed to define the cost picture for electrodepositing aluminum.

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Any discussion of this paper will appear in a Discussion Section, to be published in the December 1952 issue of the Journal.

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APPENDIX

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The Effect of Indium Sulfate in Chromium Plating Baths[1]

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ABSTRACT

Addition of indium sulfate to the regular 100 to 1 chromium plating bath permitted the formation of a bright electrodeposit at 32°C at current densities considerably above the accepted bright plating range. The deposit was more nearly crack-free than that usually formed and it was a better protective coating according to a salt drop test. It was more adherent both to steel and to copper than deposits formed from the regular bath in the bright range. Indium was present in the deposit to only a very small amount, if at all.

INTRODUCTION

In the course of an investigation (1) of vapor-deposited metal films, chromium and indium were evaporated simultaneously and the resulting metal film appeared to be free of a crack system up to 200× magnification. This was of interest because evaporated chromium films of the same thickness, about 1μ, showed a crack network typical of that seen in electrodeposited chromium. On the basis that nucleation and growth of nuclei in vapor deposition and in electrodeposition are similar processes, it was thought that an electroplate formed by codeposition of chromium and indium would be of interest. The subsequent research proved the premise to be false, but the properties of the electroplate produced were such as to warrant reporting.

As an aside, vapor deposition experiments with chromium alone gave some information bearing on Snavely's hypothesis (2) of the cause of the crack system. He suggested that face-centered or hexagonal chromium hydrides deposit and in time change to body-centered chromium and hydrogen. The change is accompanied by decrease in solid volume and formation of cracks. These fill with "cathode film" composed of partially reduced chromium-VI.

Evaporated chromium films were formed by passing current through a tungsten filament, electroplated with chromium, in a closed system at 10^{-5} mm Hg. On heating initially, there was a large increase in pressure indicating release of residual hydrogen from the electroplate. Pumping was continued until there was no longer any indication of freed gas. The chromium was then vaporized and condensed on any suitable support.

The resulting chromium film had a typical crack system in spite of the fact that the hydrogen had been driven off. Snavely's suggested mechanism seems to be adequately supported by the evidence he presented (2) but it apparently does not supply a complete answer. Perhaps oxygen is involved since there was enough, even at the low pressure, to convert an appreciable amount of chromium to one of its oxide forms.

EXPERIMENTAL PLATING BATHS AND CONDITIONS

All of the plating baths used contained 250 g/l of CrO_3 and 2.5 g/l of H_2SO_4. The several variations in composition or conditions are given in Table I.

The variations provided for comparison between the ordinary system (I), the same at lower temperature (II), the usual plating bath at the lower temperature but in the bright plating range (III), a bath containing indium-III and a chromate to sulfate ratio of 10.9 to 1 (IV), a bath containing an equivalent amount of indium but a ratio of 100 to 1 (V), and baths with a ratio of 10.9 to 1 but with no indium (VI).

The conditions for comparison are based on an investigation of the bath containing indium sulfate at concentrations between 8.0 and 38.7 g/l and at current densities between 6.2 and 17.9 amp/dm^2. Of the plates produced from this modified bath those formed at the conditions given in Table I were found to have the most desirable characteristics.

All chemicals used were of C.P. grade or better. The indium sulfate was prepared here by dissolving 99.9 per cent metallic indium in hot concentrated H_2SO_4, evaporating to dryness to remove excess acid, recrystallizing, and drying. To check whether the method of preparation had a significant effect, the salt was also prepared by crystallizing from the hot acid solution, centrifuging and washing with glacial acetic acid several times, and then drying at 250°C for 4 hours. Both preparations gave the same results. The oxide was prepared from the sulfate by precipitation with NaOH, filtering, washing thoroughly, and drying.

The anodes were of sheet lead and the cathodes were 3.9 x 2.5 x 0.10 cm coupons of copper or mild steel. The cathodes were prepared by rubbing with

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150-grit carborundum, washing with an abrasive soap, rinsing with water, and etching with dilute HNO_3 (for copper) or dilute HCl (for steel). Two anodes were used in each bath in order to plate both sides of the cathode simultaneously. The electrodes were suspended from lacquered wooden covers into 250-ml beakers. To be sure that the bath spray did not extract any material from the covers which might affect the electroplate, several covers were leached in the regular plating solution for several hours at about 60°C and the solution was then used for plating by each of the six systems. No effect was observed in any case.

Current was supplied by a d-c generator or by two 8-volt lead batteries in series. The latter were floated on a copper oxide rectifier working off the 60 cycle, 110 volt a-c house line. The output current was checked to be sure that it was free of interruption or of any a-c component. The current for the first 5 seconds of operation was about 1 amp in excess of that used during the course of the run. The circuit was always closed by immersing the electrode assembly into the solution. If these two precautions were not taken, the centers of the cathodes did not plate and in some instances corroded through.

TABLE I

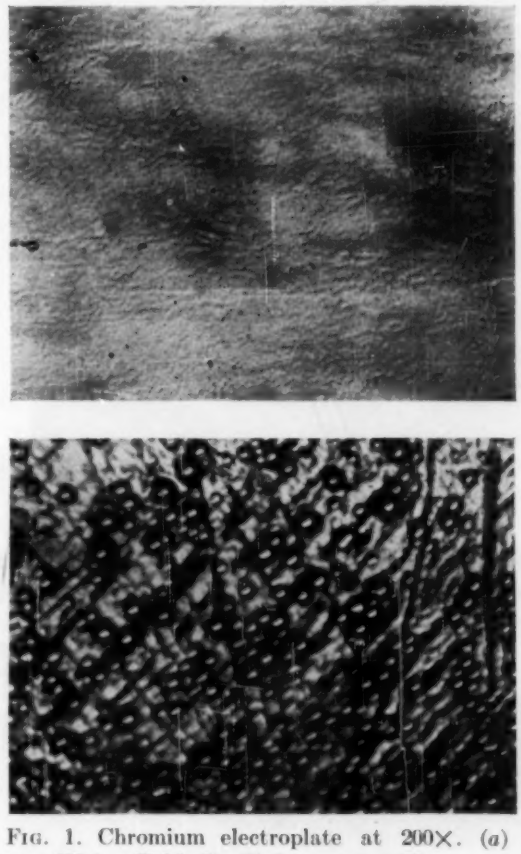
	Current density amp/dm²	Temperature °C	Additions g/l
I	16	45	—
II	14	32	—
III	4	32	—
IV	14	32	$In_2(SO_4)_3$, 38.7
V	14	32	In_2O_3, 20.8
VI	14	32	Na_2SO_4, 31.9; or H_2SO_4, 22.0; or $Fe_2(SO_4)_3$, 29.9

The plating baths were placed in a water thermostat maintained at 30° ± 0.5°C. The temperature of the plating solution rose to 32°C after about five minutes of operation and thereafter remained at that temperature. The bath *p*H, originally about 0.1, never exceeded 0.3 even after extensive use. Plating time was 12 hours in all cases. The solutions were not stirred. Plating baths were replenished periodically with particular attention being paid to the chromate content and *p*H, since indium depletion by plating was not a major factor.

The electroplates obtained from systems IV and V were analyzed by gravimetric, titrimetric, colorimetric, and polarographic methods, but none provided an accurate determination for indium content. Emission spectrographs showed the chromium lines plus a bright one at 3251.6 Å. This is the position of the brightest line of indium but the next brightest lines, at 3039.4 and 3258.6 Å, were obscured. The analytical difficulties were undoubtedly caused by the large chromium content. Although an exact value cannot be given for indium content, it is possible to state that there was definitely less than 1 per cent in any of the plates and probably very much less.

Results

The current efficiency of system IV was of the order of 10 per cent on a weight basis. The electroplates were generally uniform in cross section except at the very edges and were always of a thickness of 0.003 cm or more. The deposits obtained from this system were superior in several ways to those obtained by the others listed above. They were visibly brighter and microscopically smoother; as removed from the bath, they showed only a few fine cracks[3] at the most; they were more adherent to both copper and steel; and they provided better protective coatings. A typical electrodeposit of this system is shown in Fig. 1*a*, and one typical of system V in Fig. 1*b*. These should be compared to a system I deposit, such as the unsplit portions of Fig. 4*a* which also depict the appearance of a system III plate quite well. All are at 200× magnification.



(*a*)

(*b*)

FIG. 1. Chromium electroplate at 200×. (*a*) From system IV (see Table I), (*b*) from system V.

[3] These became slightly more apparent with age, e.g., after several weeks.

Anodic treatment in the plating bath for 5 minutes at 14 amp/dm² did not develop a crack system in the system IV deposits, but did deepen and broaden those formed from the regular baths. It was possible to develop slight cracks on system IV electroplates by anodic treatment for 5 minutes in 0.1*N* H_2SO_4 at the same current density. All electrodeposits produced were made the cathode in an acid copper sulfate plating bath and copper plated at the standard plating conditions (system I). Copper deposited along and in the crack systems where these existed originally or were developed. Specifically, fine lines

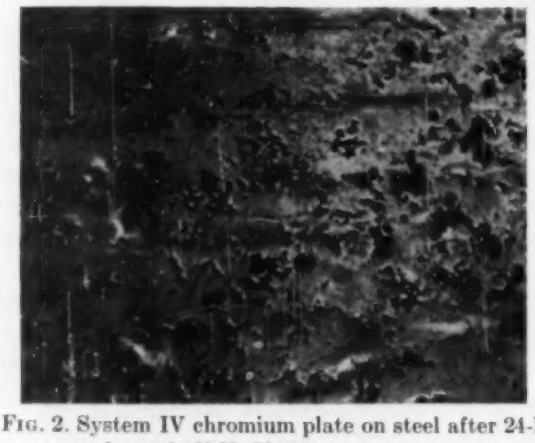


FIG. 2. System IV chromium plate on steel after 24-hour exposure to drop of 5*N* NaCl. 200×.

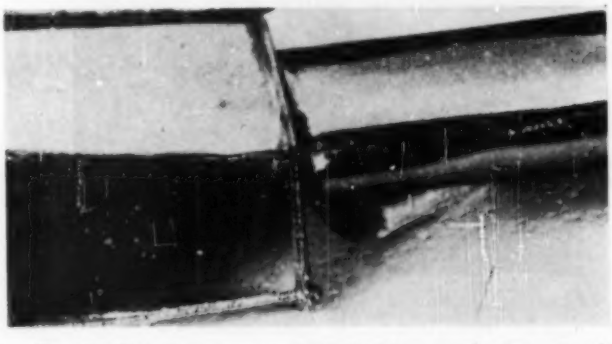
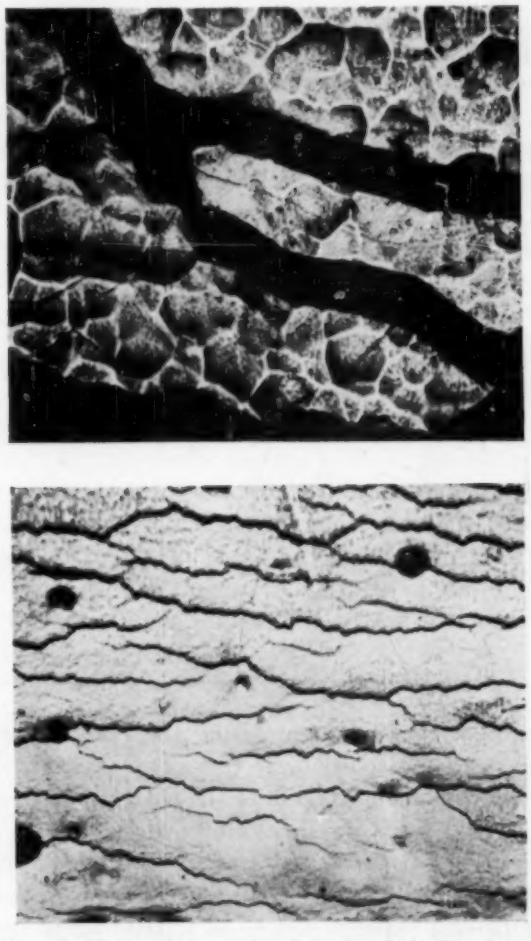


FIG. 3. Plated copper coupons bent around a 7 mm rod. *Left*—from system I, *right*—from system IV. 1.5×.

of copper were deposited on all the chromium plates except those of system IV and the copper could not be removed by vigorous wiping. On system IV deposits, occasional pinpoints of copper could be seen, but these were removable simply by blowing them off. Copper which deposited adhered well only on the system IV deposits anodically treated in sulfuric acid. Even here there was only little continuity in the copper lines.

Occasionally, pores, such as those in Fig. 4*b*, were visible at 200× magnification but the coatings showed good protective character. These were tested by putting drops of 5*N* NaCl on the surfaces of the plated steel specimens. These were allowed to stand for 24 hours in a closed container over 5*N* NaCl, the latter to prevent evaporation. The only noticeable effect on system IV deposits was slight pitting of the chromium, an observation reported previously for stripped, electrodeposited chromium (3). In general, the effect was much less than that pictured in Fig. 2, that area being by far the worst seen. With all other electroplates red rust appeared as a ridge all along the crack system.

Reflection electron-diffraction patterns of the system IV deposits gave a diffuse background with



(*a*)

(*b*)

FIG. 4. Photomicrographs of the bends in Fig. 3 at 200×. (*a*) From system I, (*b*) from system IV.

only one or two broad lines which were difficult to distinguish. Patterns for other electroplates were quite sharp and indicated the presence of well-defined and oriented crystallites. (Fig. 3*a* of Ref. 4 shows such a pattern.) Thus it may be concluded that the grain size of system IV electroplates is very small.

The system IV deposits adhered to the basis metal better than did those formed with the other systems. A comparative measure of adherence was obtained by bending the plated copper cathodes around a 7-mm diameter rod. The system IV deposits showed a few small cracks after bending through 180°. The

copper base was not visible through these cracks nor was there any evidence that the deposit had separated from the basis metal. Electroplates from systems I, III, and V began to splinter and break off when the bend reached an angle of about 45°. Fig. 3 shows typical results. Deposits from systems II and VI splintered badly and separated from the copper when bent only very slightly. Photomicrographs of the bent areas of Fig. 3 are shown in Fig. 4. All of the samples chosen for this test were of approximately the same thickness, 0.003 cm.

Discussion

The chromium electroplates described are not revolutionary in nature since smooth, bright plates have been prepared before. Also, essentially crack-free chromium deposits are described by Dubpernell (5), and others. Improvement in adhesion by addition of tervalent cations to the plating bath has been claimed (6). The interesting thing here is that the sulfate of a cation which exists only in the tripositive oxidation state exerts what appears to be a profound influence on the character of the electrodeposited metal.

Experimental evidence is not yet available to account adequately for a mechanism by which the apparently desirable properties of system IV deposits occur. The plating conditions were such as to expect dull plate, for example at 32°C the current density was far above the accepted bright plating range. The low CrO_3/H_2SO_4 ratio could not account for the properties, since addition of other sulfates to give the same ratio gave rough deposits. The indium-III ion alone does not appear to be the causative agent since the system V electroplates were dull and showed an extensive crack system. The system IV deposits were sufficiently thick so that cracks should have been as profuse as on plates from the regular plating baths.

Several possibilities to explain the effect of the indium sulfate addition were considered. One was that indium plated out of the bath first, but tests on thin deposits gave no evidence that this was so. Another was the possibility of an intermetallic compound, but this was not supported by the present work or the literature. A third was that the presence of indium prevented hydride formation, but this was followed without affirmative results. Then, the fine-grained metal led to the speculation that hydrated indium oxide, formed in the relatively alkaline cathode film, retarded grain growth. However, this was contrary to the findings that indium oxide additions were not effective. Moreover, there is no good reason to believe that this material should act differently than other tervalent oxides, e.g., chromium or iron. The same considerations apply to the possibility that In^{+++} acts as a "getter" for hydroxyl ions, that is, as a solid buffer.

There is the possibility that the indium ion acts as a regulator of sulfate ion activity which adsorbs on the cathode in competition with chromate ion (7). Since the latter is reduced directly (8), it suggests that indium ion acts as an internal regulator if the CrO_3/H_2SO_4 ratio is not too large. This is supported by the fact that, with indium sulfate concentrations from 10 to 17 g/l, there was a constant optimum current density (12.8 amp/dm²) with continually improving plate properties at the higher concentrations. This indicates that current is the controlling factor up to some concentration at which point the indium sulfate concentration becomes controlling.

Summary

Adherent, bright, protective chromium plate in thicknesses in excess of 0.003 cm was formed on steel or on copper by plating from a regular chromium plating bath to which was added 38.7 g/l of $In_2(SO_4)_3$. The conditions were: 32°C, 14 amp/dm², no stirring. The current efficiency by weight increase was about 10 per cent. At the most, only a few fine cracks were seen at 200× magnification and the plate was not nearly as rough as the usual chromium plate. A satisfactory explanation for the effect of the additive is not yet available.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1952 issue of the Journal.

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Cathode Polarization Potential during Electrodeposition of Copper

II. Variation of the Cathode Polarization Potentials with Current Density and Electrolyte Concentration[1]

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ABSTRACT

It has been shown that under comparable conditions the use of the Haring cell and the mercury reference electrode leads to similar values of the cathode polarization potential. These two methods have been used to study the variation with current density and with concentration of the total cathode polarization, concentration polarization potential, and activation overpotential of copper cathodes in copper sulfate-sulfuric acid solutions prepared by the method developed earlier (1). Even under rigidly controlled conditions of preparation there appears to be a certain instability of solutions containing high concentrations of copper sulfate, as is manifested by variations in the polarization potential on repeated electrolysis of the solution. The variation of the polarization potentials with current density is discussed in relation to theory.

Introduction

A knowledge of the effects of the copper sulfate and sulfuric acid concentrations, and hence of changes in the cupric ion activity, on the cathode polarization potential of copper was a necessary preliminary to the study of the effects of addition agents on electrodeposition baths of this type. Previous studies in this direction have been directed principally toward a consideration of the energy efficiency of copper-refining cells, and, in view of the changes in the characteristics of acid copper sulfate solutions during storage and during use (1), are somewhat difficult to interpret. It was therefore decided to reinvestigate the whole problem and to determine the separate contributions of the concentration polarization and activation overpotential under standard conditions for a wide range of bath compositions and current density.

This study involved measurements with both unstirred and stirred solutions. Of the possible methods for determining the polarization potential with stirred solutions, that of adapting the Haring cell technique, so that the solution could be agitated without interfering with the polarization measurements, was found to be difficult, and hence it was necessary to use the mercury reference electrode method for this purpose. On the other hand, for the reasons discussed earlier (1), the Haring cell yields results which have more significance when unstirred solutions are used. In view of these circumstances, and of the fact that both methods have been used frequently in previous investigations of the cathode polarization potential of copper, it was desirable to make a critical comparison of the two methods.

[1] Manuscript received August 8, 1950.

Experimental Results

Comparison of Results with the Haring Cell and Mercury Electrode

In order to obtain identical experimental conditions, simultaneous measurements were made by the two methods, using the Haring cell with the capillary of the half-cell at the center of the cathode. By using a very thin-walled capillary tube, the increase in the resistance of the cathode compartment due to its presence affected the apparent polarization potential, as determined by the Haring cell method, by only 1 mv. In making measurements with the half-cells the static equilibrium potential was determined prior to applying the current, and this value was subtracted from the dynamic value to obtain the polarization potential. All measurements were made at 25°C.

Studies were made with the "standard" electrolyte (125 g/l $CuSO_4 \cdot 5H_2O$, 50 g/l H_2SO_4) in the stable form (S_{High}), which yielded fine copper deposits and a constant state polarization potential (C.S.P.) value of 100–105 mv at 2 amp/dm², and the solution (S_{Low}) of the same composition which gave a coarse deposit and a C.S.P. value of about 50 mv. As indicated earlier (1), S_{High} and S_{Low} differ

only in that the former is freshly prepared under rigidly controlled conditions, while S_{Low} is the same solution which has been allowed to stand at room temperature for some weeks. As the properties of S_{Low} can be simulated by the addition of small amounts of other sulfur compounds to S_{High} the differences in properties are attributed to the spontaneous formation of traces of other compounds in the solution on keeping.

The results obtained with the calomel and mercurous sulfate electrodes when Method *a* (described on page 198 of Ref. 1) was used are shown in Table I. Of particular interest is the fact that, for S_{High}, measurements with the half-cell show little variation of the polarization potential with time; this would appear to justify the neglect of the time factor by many workers in this field. With S_{Low}

TABLE I. *Comparison of Haring cell with mercurous chloride and mercurous sulfate electrode*

Time (min)	Method 1					Method 2
	Polarization potential (mv)					Polarization potential (mv)
	S_{High} A	S_{High} B	S_{High} C	S_{Low} A	S_{Low} B	S_{High} C
0	108	126	108	57	88	110
1	106	120	113	103	105	119
2	102	113	111	87	110	111
4	105	109	101	54	72	106
9	110	113	97	47	61	104
13	111	111	97	45	53	104
21	112	111	96	51	60	104
26	111	107	96	51	59	102
39	111	104	96	51	59	102
48	111	102	96	51	57	102

A—Calomel electrode, B—Haring cell, C—mercurous sulfate electrode.

however, both methods show a pronounced decrease of this potential with time. In general, the constant state polarization results obtained for S_{High} with the calomel electrode were higher and not so reproducible as those obtained with the Haring cell. On the other hand, although the initial values obtained with the Haring cell and the mercurous sulfate electrode differed, the final C.S.P. values agreed reasonably well.

This finding was confirmed by the results obtained with the mercurous sulfate electrode using Method *b*, where the agreement with the values yielded by the Haring cell is very close, further confirmation being obtained of the value 100–105 mv for the C.S.P. value of S_{High} under standard conditions.

Cathode Polarization-Current Density Curves

The shape of a cathode polarization-current density curve throws considerable light on the nature of the electrode processes involved, and this method has been used by several investigators when studying the electrodeposition of metals. Gauvin and Winkler (2) found that, in the case of copper, consistent results could be obtained by making measurements of the cathode polarization potential at various current densities during deposition on a C.S.P. base produced under standard conditions.

Applying their technique, a current density of 0.02 amp/dm² was maintained for 5 min before the polarization value was measured. The current density

TABLE II. *Cathode polarization (η)—current density curves, obtained with C.S.P. bases produced at 2 amp/dm² in solution 0.5M in H_2SO_4 and 0.5M in $CuSO_4$*

Current density amp/dm²·10²	(mv) as measured by Haring cell					(mv) as measured by	
	Expt. 1		Expt. 2 (B)	Acid etched cathode (B)	Electrolytically polished cathode (B)	Haring cell (B)	Mercurous sulfate electrode (B)
	(A)	(B)					
	1*a*	1*b*	2	3	4	5	6
20	26	21	16	16	19	12	16
40	35	35	34	29	30	30	35
60	47	49	51	44	45	47	53
80	6161	62	65	61	60	62	68
100	71	70	73	74	71	72	79
120	79	79	79	80	79	80	88
140	82	85	85	84	85	86	95
160	82	89	89	89	90	90	101
180	96	93	94	93	94	94	109
200	100	97	98	98	99	103	115
220	102	100	99				
240	107	103	103				
260	113	109	109				
280	119	117	114				
300	127	126	123				
320	138	135	132				
340	149	150	145				
360	165	165	160				
380	186	186	180				
400	218	222	210				

(A) Potential (mv) at beginning of interval.
(B) Potential (mv) at end of interval.

was then increased in steps of 0.02 amp/dm², 5 min being allowed at each stage before making the measurement, up to a maximum current density of 4.0 amp/dm². The results are shown in Table II, columns 1 and 2. The values observed at 0.02 amp/dm² were usually more divergent than for higher current density owing to the influence of the base structure. This will be discussed fully in a later communication. Only slight variations in the polarization between the beginning and the end of the 5-min intervals were observed (column 1*a* and 1*b*). The results with acid-etched cathodes (column 3) are in accord with those for electrolytically polished cathodes (column 4); other bases were found to give less reproducible re-

sults and hence the former methods were used in all subsequent work.

Simultaneous determinations of the polarization-current curve with the Haring cell and mercurous sulfate electrode (Table II, columns 5 and 6) indicated that the former gave the more consistent results and was therefore used for all subsequent $I - \eta$ curves.

Measurement of Concentration Polarization (η_c) and Activation Overpotential (η_a)

Of the possible methods for making polarization measurements with stirred solutions, that of adapting the Haring cell so that the solution could be stirred without interfering with the polarization measurements was found to be difficult. The introduction of a stirrer into the cathode compartment increased the resistance of this compartment appreciably, giving an increased apparent polarization, and attempts to correct for this increase were found to be unsatisfactory. Hence it was necessary to use the half-cell for the determination of η_a and η_c.

TABLE III. *Concentration polarization at various current densities*

Current density amp/dm²·10³	"Continuous stirring" method			"Intermittent stirring" method		
	Cathode polarization		η_c by difference	Cathode polarization		η_c by difference
	Solution not stirred	Solution stirred		Solution not stirred	Solution stirred	
	mv	mv	mv	mv	mv	mv
	1	2	3	4	5	6
20	377	383	−6	386	385	1
40	386	401	−15	400	397	3
60	398	417	−19	416	411	5
80	410	427	−17	431	425	6
100	421	433	−12	444	434	10
120	432	439	−7	449	437	12
140	441	443	−2	453	439	14
160	449	447	2	459	443	16
180	457	451	6	465	447	18
200	465	454	11	472	452	20
220	471	457	14	479	455	24
240	480	459	21	486	458	28
260	487	462	25	492	462	30
280	495	464	31	500	465	35
300	501	466	35	508	466	42
320	510	467	43	515	467	48
340	519	469	50	521	469	52
360	531	469	62	437	472	65
380	550	470	80	559	474	85
400	578	470	108	593	471	122

Although measurements with the half-cell and stirred solutions gave consistent values of η_a, it was found to be unsatisfactory to subtract these values from η, obtained with the half-cell in an unstirred solution under otherwise identical conditions, to obtain η_c. Thus, for instance, at low current densities negative values of η_c were obtained by this method of subtracting two results obtained by independent measurements (Table III, columns 1, 2, and 3). A procedure involving intermittent stirring was therefore used in which η_c was obtained directly by two consecutive measurements. Beginning at 0.02 amp/dm² the current was applied for 5 min without stirring the solution, and the polarization value was measured. The stirrer was then started and the polarization potential read again as soon as this became constant. Agitation was then stopped, the current density increased to 0.04 amp/dm², and the procedure repeated. Stirring for 1–5 sec was usually sufficient for a steady value of the polarization to be obtained at low current density, but at 3–4 amp/dm² stirring for about 30 sec was necessary for this purpose. The difference between the potentials with the solution stirred and unstirred gave η_c (Table III, columns 4, 5, and 6). In all cases the speed of the stirrer was so adjusted that if increased further it produced no significant difference in the results.

TABLE IV. *Effect of copper sulfate and sulfuric acid concentration on the C.S.P. potential*

No.	H_2SO_4 g/liter	$CuSO_4$ g/liter	1st run	2nd repeat	3rd repeat	4th repeat
			η (mv)	η (mv)	η (mv)	η (mv)
1	0	125	22	22	—	—
2	25	125	70	68	69	—
3	50	125	96	101	—	—
4	50	125	94	101	105	105
5	100	125	108	110	—	—
6	100	125	105	114	—	—
7	100	125	112	113	—	—
8	200	125	120	136	144	145
9	200	125	120	137	—	—
10	50	250	64(C)	55(C)	83(F)	86(F)
11	50	250	66(C)	71(C)	77	78(SC)
12	100	250	48(C)	100(F)	—	
13	100	250	90	98	—	
14	100	250	59	108	—	
15	100	250	88	96	—	
16	150	250	67	85	90	

F—Fine, C—coarse, SC—semicoarse (homogeneous structure intermediate between fine and coarse).

The Effects of Copper Sulfate and Sulfuric Acid Concentrations—C.S.P. Determinations

These were carried out under the standard conditions using electrolytically polished cathodes and solutions prepared by the technique described earlier (1). The same solutions were each re-used repeatedly with fresh cathodes to test whether this caused any change in the C.S.P. value. The results are shown in Table IV. With a solution containing 125 g/l $CuSO_4 \cdot 5H_2O$ and no added acid, the C.S.P. value

was comparatively small; the deposit was very coarsely crystalline resembling that from S_{Low}, the preferential growth of the crystals being parallel to the face of the cathode. Addition of acid caused an appreciable increase in polarization, but a change from 25 to 200 g/l of H_2SO_4 caused only a relatively smaller further increase. With 125 g/l $CuSO_4 \cdot 5H_2O$ all the deposits formed from solutions containing added acid were finely crystalline.

The results in Table IV show that, in spite of the precautions taken, there is still a certain element of uncertainty in the values obtained, as different

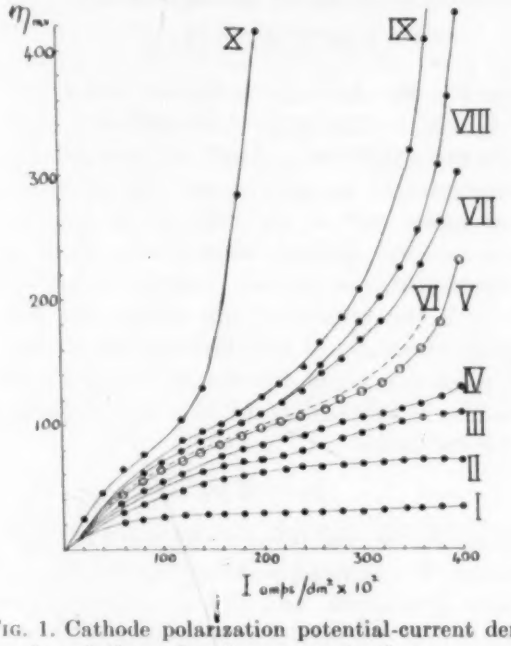

FIG. 1. Cathode polarization potential-current density curves for solutions of various concentrations.

I 0.5*M* $CuSO_4$
II 1.0*M* $CuSO_4$; 0.5*M* H_2SO_4
III 1.0*M* $CuSO_4$; 1.0*M* H_2SO_4
IV 1.0*M* $CuSO_4$; 1.5*M* H_2SO_4
V 0.5*M* $CuSO_4$; 0.5*M* H_2SO_4 ("standard" solution)
VI Derived curve for standard solution
VII 0.5*M* $CuSO_4$; 1.0*M* H_2SO_4
VIII 0.5*M* $CuSO_4$; 1.5*M* H_2SO_4
IX 0.5*M* $CuSO_4$; 2.0*M* H_2SO_4
X 0.25*M* $CuSO_4$; 0.5*M* H_2SO_4

results are obtained after previous electrolysis. This again is comparable to the "aging" required to produce optimum results in commercial plating baths. The standard solution (125 g/l $CuSO_4$; 50 g/l H_2SO_4) shows this effect least of all and was thus selected for further studies in preference to the other compositions. It might be supposed that this effect again could be explained on the basis of enrichment of the electrolyte in cuprous ion as electrolysis proceeds, but equilibrating the electrolytes prior to electrolysis by shaking with copper powder was without effect. It can be seen that not only are the polarization values increased on re-using the solutions, but the crystal structure changes also from coarse to fine. The semicoarse structure referred to in the fourth repeat usage of No. 11 solution is of interest in probably representing the actual transition stage from coarse to fine.

Polarization-Current Curves

Polarization curves for solutions containing various concentrations of copper sulfate and sulfuric acid, prepared under standard conditions, are shown in Fig. 1. For the electrolyte containing 125 g/l of $CuSO_4 \cdot 5H_2O$ and no H_2SO_4 (curve I) the low constant value of η seems to be associated with crystal

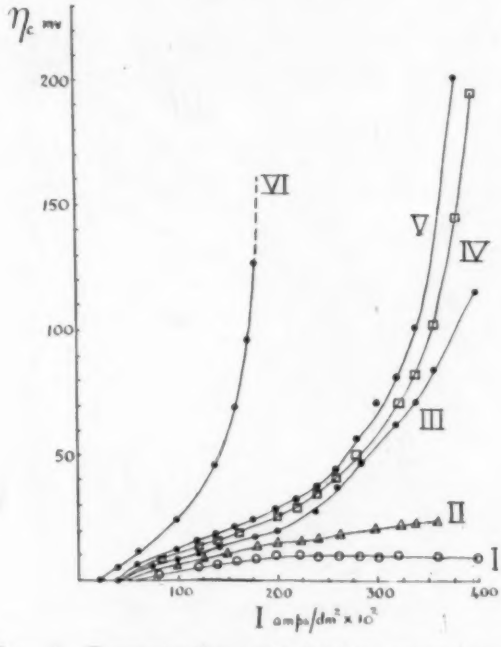

FIG. 2. Concentration polarization potential-current density curves.

I 1.0*M* $CuSO_4$; 0.5*M* H_2SO_4
II 1.0*M* $CuSO_4$; 1.0*M* H_2SO_4
III 0.5*M* $CuSO_4$; 0.5*M* H_2SO_4
IV 0.5*M* $CuSO_4$; 1.0*M* H_2SO_4
V 0.5*M* $CuSO_4$; 1.5*M* H_2SO_4
VI 0.25*M* $CuSO_4$; 0.5*M* H_2SO_4

development parallel with the surface of the cathode base, the deposit being particularly coarse.

Similar curves are obtained with higher concentrations of copper sulfate in the presence of added acid; the copper ion concentration appears to be sufficient to permit it to diffuse rapidly into the cathode film and thereby prevent excessive polarization due to concentration changes. This is confirmed by the concentration polarization-current curves (Fig. 2, curves I and II) which show that, with 250 g/l $CuSO_4 \cdot 5H_2O$, η_c does not exceed 20 mv at 4 amp/dm²; in fact with high copper sulfate concentrations, both η_a and η_c are low.

With 125 g/l $CuSO_4 \cdot 5H_2O$ and 50 or 75 g/l

H_2SO_4 there is a pronounced tendency for the total polarization-current curve to rise at high current density. This trend is reduced in the activation polarization-current curves (Fig. 3), indicating that for these electrolytes at high current density, the polarization is due largely to concentration changes.

Discussion and Interpretation of Results

Whatever is the nature of the ionic reactions at the cathode, i.e., whether it is the cupric or cuprous ions or both which participate in the electrode process, it is evident that the curves for η_a and η_c, and hence the curve for η, should be capable of

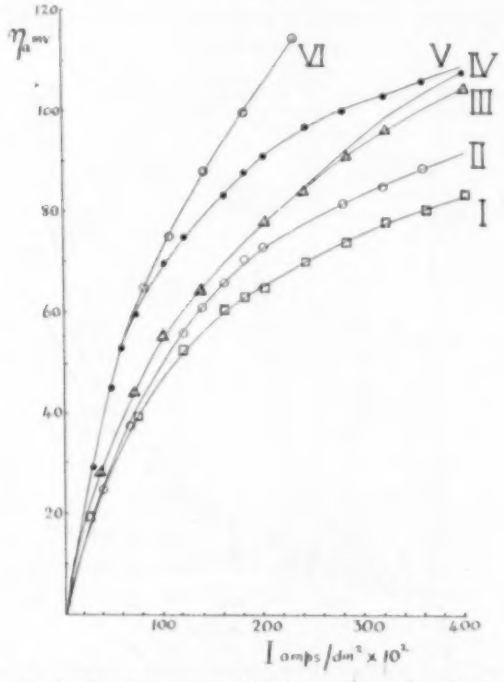

Fig. 3. Activation overpotential-current density curves

I 1.0*M* $CuSO_4$; 0.5*M* H_2SO_4
II 0.5*M* $CuSO_4$; 0.5*M* H_2SO_4
III 0.5*M* $CuSO_4$; 1.0*M* H_2SO_4
IV 0.5*M* $CuSO_4$; 1.5*M* H_2SO_4
V 0.25*M* $CuSO_4$; 0.5*M* H_2SO_4
VI 0.125*M* $CuSO_4$; 0.5*M* H_2SO_4

interpretation on the basis of the activities of the ions concerned. These will depend upon both the copper sulfate and sulfuric acid concentrations.

At low current density η_c is relatively small and the form of the total polarization-current curve will depend upon whether crystal growth or nucleus formation is the more favored process. The former will be aided by high copper ion activity, i.e., high copper sulfate and low sulfuric acid concentration. At higher current density, η will be determined largely by η_c. These generalizations have been substantiated experimentally.

Concentration polarization.—Concentration polarization has been treated theoretically by Agar and Bowden (3) in connection with hydrogen discharge and by Glasstone and Hickling (4) in respect to oxidation-reduction reactions. In both these processes, however, the cathode surface remains unchanged, and any attempt to apply their results is complicated by the fact that in the present instance metal deposition is occurring and the surface area of the copper cathode changes continuously, so that the true current density is uncertain.

From the concept of the diffusion layer and by application of Fick's law of diffusion, Agar and Bowden deduced that in the steady state the cathode conditions are given by the relationship

$$I/z\mathbf{F} = k(c_0 - c_e)/\delta \qquad \text{(I)}$$

where k is the diffusion coefficient (about 10^{-5} cm^2 sec^{-2}), δ is the thickness of the diffusion layer (approximately 0.05 cm and not varying greatly with concentration), c_0 and c_e are the concentrations (gram moles/cm^3) in the bulk of the solution and at the electrode surface, respectively, of the ions to be discharged, I is the true current density (amp/cm^2), z is the valency of the cation, and $\mathbf{F}$ is the Faraday constant. At the "limiting current density" (I_0), when the rate of diffusion is no longer sufficient to maintain the supply of ions to be discharged, $c_e = 0$ and hence

$$I_0 = z\mathbf{F}kc_0/\delta. \qquad \text{(II)}$$

With a solution containing metal and hydrogen ions, discharge of hydrogen occurs as the limiting current density is reached, and this is associated with a sharp rise in the polarization potential. From equations (I) and (II) it follows that the concentration polarization at 25°C is given by

$$\eta_c = \frac{0.059}{z}\log_{10}\frac{c_e}{c_0} = \frac{0.059}{z}\log_{10}\left(1 - \frac{I}{I_0}\right). \qquad \text{(III)}$$

A plot of η_c against $\log_{10}(1 - I/I_0)$ should therefore be linear.

Equation (II), based purely upon diffusion, should be applicable to the present case, as, owing to the high concentration of hydrogen ions, there will be practically no ionic migration of cupric ion. Substituting the appropriate values for the electrolyte 0.25*M* in copper sulfate and 0.5*M* in sulfuric acid, and taking $k\mathbf{F}/\delta$ as 20 amp/cm^2 we obtain

$$I_0 = 2 \cdot 20 \cdot 0.25 \cdot 100/1000 = 1.0 \text{ amp/dm}^2.$$

The polarization-current curve (Fig. 2) shows that for this solution (curve IV) there is a fairly abrupt change in the slope of the curve at about 1.4 amp/dm^2, while for the solution of the same sulfuric acid concentration, but 0.5*M* in copper sulfate (curve III), the sudden increase is less distinct but appears at about 3.2–3.6 amp/dm^2. With a solution

1.0M in copper sulfate and of the same acid concentration a limiting current density is not apparent in the range of current densities studied.

The discrepancies between the theoretical and observed I_0 values may arise either from the assumptions made regarding the activities of the ions or from the circumstance that the true surface area is greater than the apparent value and changes as deposition proceeds. The latter is the more probable, as satisfactory results have been obtained using this expression in relation to the oxidation of ferrous ion to ferric ion in the presence of hydrochloric acid (6). In this case, where no metal deposition occurs and the cathode surface remains constant, I_0 is proportional to the concentration. In the present case doubling the copper ion concentration approximately doubles the value of I_0, although accurate values of the latter are difficult to obtain from the curves, and the I_0 value for the solution

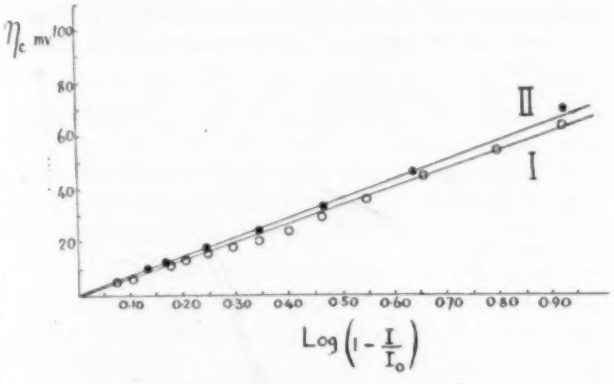

FIG. 4. Concentration polarization
I 0.5M $CuSO_4$; 0.5M H_2SO_4
II 0.25M $CuSO_4$; 0.5M H_2SO_4

1.0M in copper sulfate would appear to be at 6.4 amp/dm².

Considering the experimental difficulties and the assumptions made, the linearity of the plot of η_c against $\log_{10}\left(1-\frac{I}{I_0}\right)$ (Fig. 4) is reasonably good. The slope of this line is 0.068, which would suggest that z in equation (III) is approximately unity, but as these measurements are concerned with a dynamic problem very different from that involved, for instance, in hydrogen deposition or in oxidation-reduction processes where no metal is deposited, it is felt that no theoretical significance can be attached to this result.

Activation overpotential.—As the Tafel relationship (5) can be written in the form

$$\eta_a = a + b \log I \qquad \text{(V)}$$

a plot of η_a against $\log_{10}I$ should be linear, but the application of this expression is subject to the same limitations as in the case of η_c, and only the apparent values of I can be used.

As this overpotential arises through the slowness of one of the reactions involved in the deposition process, it would be expected that the variation of η_a with I would be determined by the nature of the process controlling the rate of deposition. In studies of the relationship between crystal structure and cathode polarization Boulach (7) found that when η_c was eliminated by using a high speed rotating cylindrical cathode η_a varied according to the relationship

$$\eta_a = \frac{RT}{z\mathbf{F}} \ln (1 + AI^x) \qquad \text{(VI)}$$

where I is the apparent current density, and A and x are empirical constants which vary with the temperature and composition of the electrolyte and with the rate of stirring. Boulach suggested that the polarization is due not only to a decrease in the activity of the copper ions in the cathode film owing to a decrease in their concentration, but also to a considerable increase in the concentration of less electropositive cations, particularly hydrogen ions. This view is in accord with the Interference Theory of Hunt (8), who suggested that the polarization is a function of the ratio of the ions to be deposited to the total number of cations in the cathode film.

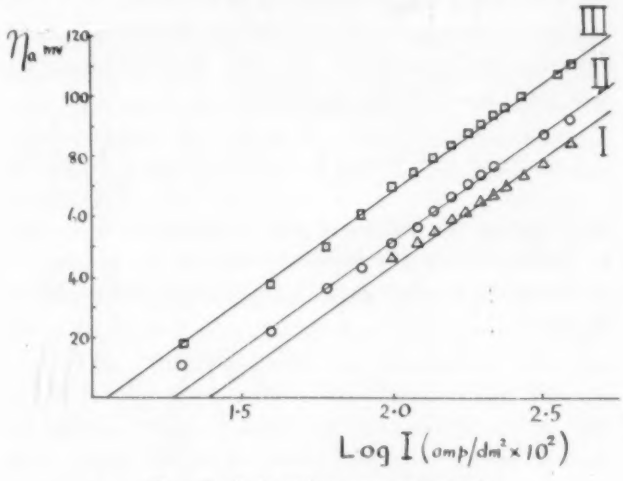

FIG. 5. Activation overpotential
I 1.0M $CuSO_4$; 0.5M H_2SO_4
II 0.5M $CuSO_4$; 0.5M H_2SO_4
III 0.25M $CuSO_4$; 0.5M H_2SO_4

For large values of AI^x equation (VI) becomes

$$\eta_a = \frac{RT}{z\mathbf{F}} \ln A + \frac{RT}{z\mathbf{F}} x \ln I$$

which corresponds with the Tafel relationship.

For 0.25M and 0.5M $CuSO_4$ the curves of η_a against $\log_{10}I$ are linear (Fig. 5, curves III and II) and the crystal form of the deposits obtained

when the solution is $0.5M$ in H_2SO_4 makes it apparent that this is associated with the frequent formation of new nuclei. Only at current densities less than 0.6 amp/dm² is η_a approximately linear with I (Fig. 3), a condition which indicates the building up of existing grains (9). With a solution $1.0M$ in $CuSO_4$ and $0.5M$ in H_2SO_4, the linearity of η_a with $\log I$ is not quite so satisfactory and the best straight line through the experimental points would have a slope slightly different from that shown, which is drawn parallel to the lines for the other concentrations. This may be associated with the large deviation of the true surface area from its apparent value. For $0.5M$ $CuSO_4$ containing no added acid η, and hence η_a, remains almost constant with increasing current density (Fig. 1) and, from the nature of the deposit, it is evident that the development of the individual lattice planes is unhindered.

Derived expression for the total polarization-current curve.—Combination of the two relationships (V) and (III) leads to the expression

$$\eta = \eta_a + \eta_c = a + b \log_{10} I + c \log_{10}\left(1 - \frac{I}{I_0}\right). \quad \text{(VII)}$$

Introducing the values of the constants a, b, c, and I_0 derived from the separate studies of η_a and η_c we have for a solution $0.5M$ in $CuSO_4$ and $0.5M$ in H_2SO_4

$$\eta = -0.050 + 0.071 \log_{10} I + 0.068 \log_{10}\left(1 - \frac{I}{3.6}\right).$$

Values of η calculated from this equation are in accord with observation for a current density of 0.2–3.0 amp/dm² (Fig. 1, curve VI). Divergences for the initial values at 0.2 amp/dm² are due to the effect of the base on the initial layers of atoms deposited, while the deviations above 3.0 amp/dm₂ can be attributed to difficulty in obtaining accurate values of η_a and η_c at such high current density.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1952 issue of the JOURNAL.

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The Effect of Chloride Ions on Copper Deposition[1, 2]

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ABSTRACT

Addition of chloride ions to an acidified copper sulfate solution had no effect on the electrode processes below a definite minimum concentration, corresponding to the precipitation of cuprous chloride. The latter was adsorbed by the deposit and acted as a mild addition agent, decreasing the grain size with a corresponding increase in hardness and reflectivity of the deposit, and a small increase in polarization. Increased powder formation and, at high chloride concentration, formation of cuprous chloride were noted at the anode. The general behavior was not affected by the addition of bindarine to the electrolyte, but gelatin considerably increased the powder formation, the latter being maximal at given chloride and gelatin concentrations, and prevented the chloride from entering the deposit, presumably due to the formation of a gelatin-cuprous chloride complex.

Introduction

Addition of chlorides (NaCl or HCl) to acidified copper sulfate electrolytes has been common practice in copper refineries for many years. Indeed, their presence may be considered essential, since it keeps the silver ion concentration very low, and minimizes the codeposition of antimony and bismuth with copper. The chloride concentration used is usually from 10 to 50 mg/l (1, 2).

Little information is available on the effect of chloride ion on copper deposition. It has been reported that the presence of chloride decreases the grain size of the deposit (3), though this has been contradicted (4); while an increase in chloride ion concentration from 0 to 0.12 g/l has been stated to cause a slight decrease in cathode polarization, without change in the anode polarization (4). It has also been reported that addition of chloride ions to electrolytes containing sulfite liquor as addition agent prevents brittleness of the copper deposit (5).

The most thorough investigation was published by Yao in 1944 (6). Working with pure acidified electrolytes, in the absence of addition agents, he found that an increase of concentration at low chloride concentrations resulted in small increases in cathode polarization and Vickers Hardness Number, and a large decrease in the grain size. At concentrations greater than about 15 mg/l, however, cathode polarization and hardness decreased sharply with chloride concentration, while an increase in grain size was observed.

[1] Manuscript received April 23, 1951. This paper prepared for delivery before the Detroit Meeting, October 9 to 12, 1951.

[2] Contribution from the Physical Chemistry Laboratory, McGill University, with financial assistance from the National Research Council of Canada.

The present study was made in view of the many aspects of copper deposition in the presence of chloride that still require explanation, and in particular to determine the effect of chloride in the presence of addition agents, about which no information was available in the literature.

Experimental

Reagent grade copper sulfate pentahydrate, sulfuric acid, and sodium chloride were used throughout. The composition of the electrolyte was the same for all experiments, and consisted of 125 g/l of copper sulfate pentahydrate and 150 g/l of sulfuric acid. Deposits were obtained on a cathode between two anodes of high purity at a current density of 2 amp/dm^2. Glass battery jars were used, and no agitation was provided. The same precautions observed in previous studies (7–9) were again followed for preparing and cleaning the electrodes, and for drying the deposits. Chloride concentrations were determined potentiometrically, using a silver-silver chloride electrode as reference electrode. This method was also used in the presence of addition agents, since recently published results (10) confirm earlier conclusions (11) and indicate that the accuracy of the method is little affected by proteins.

The effects of chloride were studied with gelatin and with bindarine present in the electrolyte. Both substances are commonly used in copper refining, the former as glue, the latter as a by-product of the sulfite pulp industry containing 50 to 60 per cent calcium lignosulfonate as the active material.

Results

In preliminary experiments, it was observed that addition of chloride ion as sodium chloride to the electrolyte had no obvious effect on deposition be-

low a minimum concentration, which was quite reproducible and amounted to 9 mg/l at 25°C and about 19 mg/l at 50°C. Above this minimum concentration, the deposits became finer grained and gradually changed to a salmon pink color. Increased concentrations gave increased fineness to the structure.

Above the minimum concentration, the anode processes were also affected. Corrosion was more irregular and pitting and irregular depressions were frequently observed. Differences in thickness showed that solution occurred mainly from the upper part of the anodes. A great deal of very fine copper powder

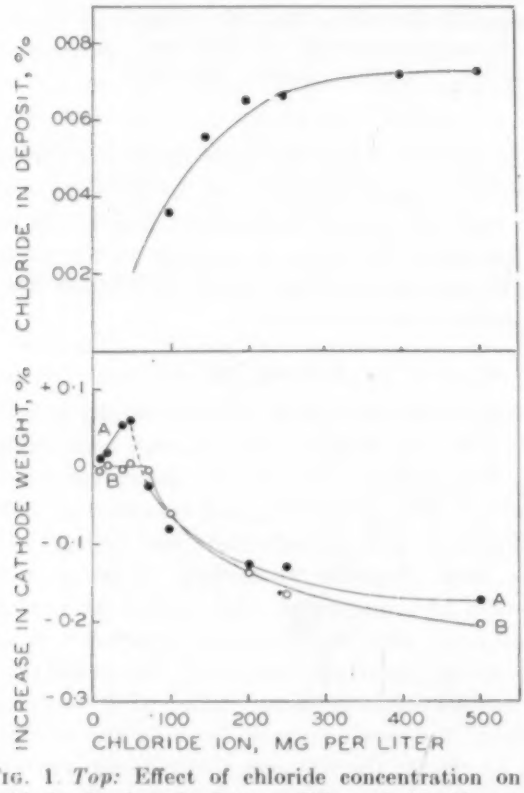

FIG. 1. *Top:* Effect of chloride concentration on the chloride in the deposit. *Bottom:* Effect of chloride concentration on the cathode excess weight (A) in the absence of addition agent; (B) in the presence of gelatin.

was found to accumulate directly under the latter at the bottom of the cells, at both 25° and 50°C. At still larger concentrations, less and less copper powder was formed, but a grayish white precipitate began to appear on the anodes, partially covering them, and slowly accumulating in the cells in the form of very thin flakes. Analysis showed that this material was cuprous chloride. At sufficiently high concentrations of chloride, the film completely surrounded the anodes, and increased the anode polarization severely. Analysis of the electrolyte showed that the chloride ion concentration became depleted at a fairly rapid rate especially at higher concentrations. These effects were shown to be due to chloride ion rather than sodium ion by the observation that addition of sodium sulfate instead of sodium chloride had no effect on the electrode processes, even after prolonged electrolysis.

Presence of Chloride in the Deposits

Large deposits (avg wt 22.7 g) were obtained in the presence of increasing amounts of chloride and were stripped off the cathode which had been previously dipped in a solution of beeswax in carbon tetrachloride. The deposits were dissolved in 50 per cent nitric acid, and their chloride content determined electrometrically with the results shown in Fig. 1, top.

Identical determinations when 50 mg of bindarine was present in the electrolyte showed that, within the experimental error, the amount of chloride entering the deposit was not affected by this addition agent. On the other hand, deposits obtained in the presence of 10 and 50 mg/l of gelatin contained no chloride at the lower chloride concentrations, and only traces could be detected at chloride concentrations above 300 mg/l.

Increase in Weight of Cathode Deposits

The excess weights of copper deposits obtained in the presence of increasing amounts of chloride ions were determined relative to the weight of a deposit obtained in series under the same conditions, but in the absence of these ions. The results, expressed on the basis of the weight of the deposit in the coulometer in series, are shown in curve A, Fig. 1, bottom, for a temperature of 25°C. Addition of 50 mg/l of bindarine to the system did not in any way affect these results, but addition of 50 mg/l of gelatin (curve B, Fig. 1) caused no increase in the excess weight at low concentration and gave a sharp decrease in cathode weight at concentrations above 100 mg/l.

Reflectivity and Physical Appearance of Deposits

A previous study of the reflectivity of copper deposits (12) has shown that this property is very sensitive to minute changes in crystal size and orientation. The change in the reflectivity of the deposit caused by an increase in the chloride content of the electrolyte was determined relative to a polished silver standard, with the results shown in Fig. 2, top. A definite increase in reflectivity was observed up to a concentration of approximately 100 mg/l. The slight decrease at higher concentrations is probably not to be ascribed to an increase in crystal size, but to an increased roughening of the surface and the appearance of irregularities on the deposits, even after a short period of deposition.

Gelatin increases the reflectivity of copper deposits to a considerable extent (12) and addition of chlorides in concentrations up to 100 mg/l did not decrease it. At higher concentrations, however, irregularities and excrescences began to appear, which decreased the reflectivity. Bindarine, on the other hand, when present alone in an electrolyte (12) increases the reflectivity to an extent comparable with that for chloride in Fig. 2. No appreciable changes were observed when chloride was added, except that at high chloride concentrations, deep convection current lines and irregularities were again observed in the deposits.

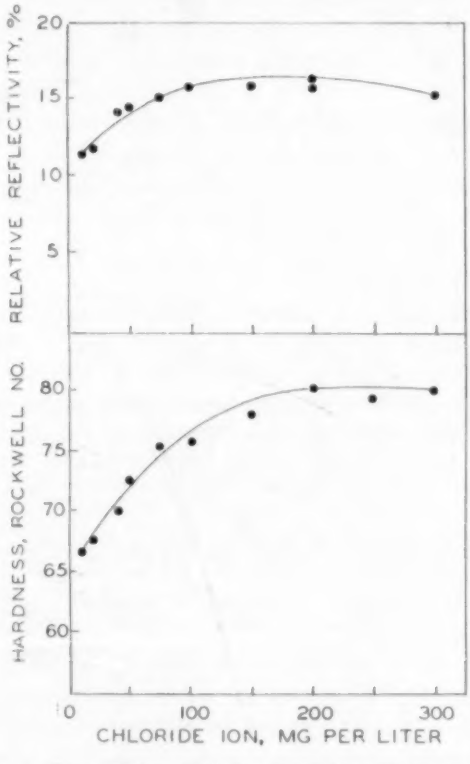

FIG. 2. *Top:* Effect of chloride concentration on the reflectivity of the deposit. *Bottom:* Effect of chloride concentration on the hardness of the deposit.

Hardness of Deposits

In Fig. 2, bottom, is plotted the relation between chloride concentration and hardness of the deposit as obtained with a Rockwell Hardness Tester, using a $\frac{1}{8}$-in. penetrator and 60-kg load, due precautions being taken to minimize the effect of the base metal. The maximum effect is comparable with that when the electrolyte contained 50 mg/l of bindarine alone (82 Rockwell Number), but considerably smaller than that when the electrolyte contained gelatin (a Rockwell Number of 90.5 for 20 mg/l of gelatin). As with reflectivity, the hardness of deposits obtained in the presence of gelatin or bindarine is not affected when chlorides are added to the electrolyte.

Cathode Polarization

Measurements of the anode and cathode polarizations are most easily made in a Haring cell (13) with good accuracy and reproducibility of results, providing the same initial surface is always used, and sufficient time is allowed for steady state values to be reached (7). Starting with an initial cathode surface deposited at 25°C at an apparent current density of 2 amp/dm^2, the rate of attainment of steady state polarization values in the presence of various amounts of chloride is shown by the typical curves in Fig. 3. It should be noted that the values observed after a few minutes of electrolysis—a procedure which was followed by Yao (6)—are considerably different from the final steady state values. The effect of chloride ion on the steady state cathode polarization is also shown in Fig. 3.

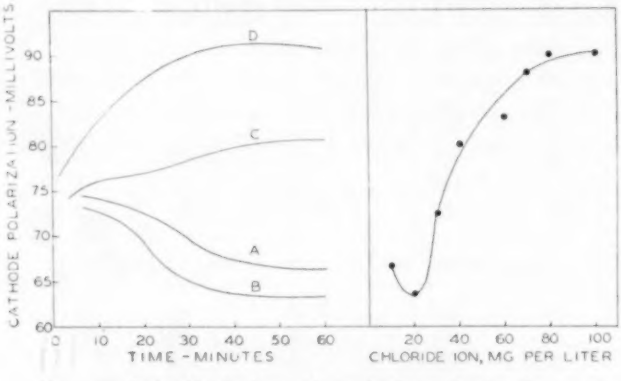

FIG. 3. *Left:* Variation of cathode polarization with time, in the presence of (A) 10 mg, (B) 20 mg, (C) 40 mg, and (D) 100 mg per liter of chloride ion. *Right:* Variation of steady state cathode polarization with chloride ion concentration.

No effect on the polarization measured in the presence of 5 mg/l of gelatin, or of 50 mg/l bindarine, was observed when 100 mg/l of chloride ion was added to the electrolyte.

Anode Solution, Copper Powder, and Cuprous Chloride Formation

In an effort to explain some of these results, a study was made of the effects of increased chloride concentrations on the rate of solution of the anodes, and on the formation of copper powder and cuprous chloride. The extent of solution of the anodes was found by direct weighing. At the end of the deposition, the electrolyte was filtered through a tared sintered glass crucible, the powder and precipitate washed with small portions of dilute sulfurous acid, dried, and weighed. The total weight of copper powder and cuprous chloride was thus obtained. The cuprous chloride was then dissolved, the copper powder weighed, and the weight of cuprous chloride

obtained by difference. The extent of anode solution and of copper powder and cuprous chloride formation (the latter in terms of its copper content) were calculated on the basis of the weight of the copper deposited on the cathode in the coulometer in series. The results are given in Table I. The peculiar behavior of anode corrosion in presence of chloride ions has already been mentioned, but it was particularly unusual at 2°C, at which temperature the lower part of the anode was covered with a pinkish zone, very even and smooth, strongly reminiscent of the appearance of an electrodeposit, and considerably thicker than the rest of the electrode.

TABLE I. *Copper powder and cuprous chloride formation*

Chloride ion in solution mg/l	Anode solution %	Copper powder %	CuCl precipitate %	Copper in CuCl %
Temperature: 25°C. Current density: 2 amp/dm²				
0	100.7	0.22	—	—
10	102.6	1.93	—	—
30	102.6	1.96	—	—
50	102.4	1.75	—	—
100	101.5	0.68	0.405	0.26
250	102.3	0.22	3.07	1.97
500	103.1	0.16	3.78	2.43
Temperature: 50°C. Current density: 2 amp/dm²				
0	102.1	0.28	—	—
30	103.3	1.43	—	—
50	103.5	1.52	—	—
100	103.2	1.22	0.11	0.07
250	104.0	0.34	2.20	1.41
500	104.6	0.21	3.47	2.23
Temperature: 2°C. Current density: 1 amp/dm²				
0	100.1	0.05	—	—
0	100.1	0.04	—	—
50	104.9	4.75	—	—
50	104.1	3.70	0.125	0.08
100	102.8	0.39	3.27	2.09
100	102.9	0.67	3.22	2.07

Table I shows that, without addition of chloride ion, the powder formation was quite small and increased with temperature. In the presence of chloride, the powder formation passed through a maximum at a given temperature, then decreased sharply, while the cuprous chloride formation increased. Maximum copper powder formation also seemed to decrease as the temperature increased. Finally, the difference between the amount of anode dissolved and the sum of copper going to powder and to cuprous chloride remained approximately constant at a given temperature.

Results obtained with increasing amounts of chloride ions and a fixed amount of bindarine (50 mg/l) indicated that, within the experimental error, the anode processes were not altered by the presence of bindarine. In the presence of 50 mg of gelatin, Fig. 4 shows the same trends as in the absence of addition agent, with the striking exception that the copper powder formation was now considerably greater, representing 33.8 per cent of the coulometer deposit weight for the optimum concentration of 50 mg/l of chloride. Keeping the chloride at the latter concentration, an even greater yield amounting to 39.5 per cent of the coulometer deposit, could be obtained

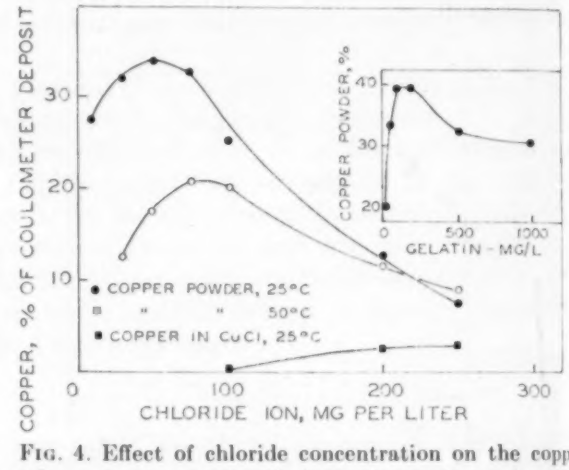

FIG. 4. Effect of chloride concentration on the copper powder and cuprous chloride formation in the presence of gelatin. *Insert:* Copper powder formation in the presence of 50 mg/l of chloride ion and varying amounts of gelatin.

TABLE II. *Anode polarization in presence of chloride ions*

Chloride ions mg/l	Gelatin mg/l	Bindarine mg/l	Deposition hr	Anode polarization mv
0	—	—	1	31.5
100	—	—	5	65.2
500	—	—	5	431.9
500	—	—	8	532.3
100	—	50	5	94.3
500	—	50	5	387.0
500	20	—	5	1050

with 200 mg/l of gelatin, as shown by the insert in Fig. 4.

Anode Polarization

Measurements of the anode polarization showed that at 25°C and 2 amp/dm², chloride ion had no effect whatever until cuprous chloride formed, above the minimum chloride concentration required. It then rose slowly, with marked irregularities when flakes of cuprous chloride became detached from the anode. It was observed to increase more regularly when a complete film of cuprous chloride surrounded the anodes. Table II shows values of the anode polarization at different times of deposition and for

different electrolytes. The first value, in the absence of chloride ion, is a steady state value which remains essentially constant after the first hour of deposition. The other values showed marked fluctuations as deposition progressed and are given merely to indicate the order of magnitude. It should be mentioned that the partial passivity indicated by the high polarization values, especially in the presence of gelatin, merely reflects the increase in potential needed to maintain a given current density with increased resistance of the cuprous chloride film.

Discussion

Careful consideration of the mechanism of copper deposition from sulfate solutions is required before a satisfactory explanation for some of the results presented can be offered.

If a sheet of copper is immersed in a copper sulfate solution, in the absence of any chlorides or addition agents, the following reaction will occur until equilibrium prevails at the metal-solution interface:

$$Cu^{++} + Cu \rightleftarrows 2Cu^{+}. \qquad (I)$$

From the equilibrium constant for this reaction (14–16), it can be calculated that the equilibrium concentration of cuprous ions in the body of a 0.5 molar copper sulfate solution, such as that used in this investigation, would be close to $0.87 \cdot 10^{-3}$ gram mole/l at 25°C. In the absence of the metal or of a suitable process to maintain the cuprous ion concentration, the latter will continuously decrease, owing to oxidation by dissolved atmospheric oxygen in acidic solutions, or through hydrolysis (17). Similarly, it is possible to estimate (18) the equilibrium concentration of cuprous ions in the anode film to be approximately $1 \cdot 10^{-3}$ gram mole/l and that in the cathode film to be approximately $0.65 \cdot 10^{-3}$ gram mole/l under the operating conditions used. The fact that the cuprous ions are likely to be present in the form of the complex $(CuSO_4)^-$ does not in any way alter this discussion.

If chloride ions are now added to an equilibrium solution of cupric and cuprous ions still without electrolysis, formation of the little soluble CuCl proceeds according to the equation

$$Cu^{+} + Cl^{-} \rightleftarrows CuCl. \qquad (II)$$

Using $2.2 \cdot 10^{-7}$ as the value of the solubility product constant at 25°C (14), it can be calculated that for a 0.5 molar copper sulfate solution, precipitation of CuCl will commence when the concentration of chloride ion is greater than $2.5 \cdot 10^{-4}$ gram mole/l, or 8.9 mg/l. The experimental observation that deposition begins to be affected by the presence of chloride ion at approximately this concentration gives strong reason to assume that CuCl, still in colloidal form since it has had no time to grow into a visible precipitate, is responsible for the addition agent effect of chlorides. This is further supported by the adsorption type of curve for the chloride content of the deposit (Fig. 1). The solubility product constant at 50°C could not be obtained from published data, but can be estimated to be $1.2 \cdot 10^{-6}$ from the minimum concentration that will affect deposition at this temperature. It must be particularly noted that solution of CuCl to form the complex ion $(CuCl_2)^-$ according to the equation

$$CuCl + Cl^{-} \rightleftarrows (CuCl_2)^{-} \qquad (III)$$

can occur to appreciable extent only in the presence of considerably larger concentration of chloride ions than was used in this investigation (17, 19–21).

The Anode Processes

So far, only equilibrium conditions in the absence of electrolysis have been considered. If the processes occurring at the anode during electrolysis in the absence of chloride or addition agents are now examined, the following three reactions are possible:

$$Cu \rightarrow Cu^{++} + 2e, \qquad (IV)$$

$$Cu \rightarrow Cu^{+} + e, \qquad (V)$$

$$Cu^{+} \rightarrow Cu^{++} + e. \qquad (VI)$$

Equation (IV) predominates during anodic solution. Since the anode film contains cuprous ions in concentration higher than in the solution, these ions pass by migration and diffusion across the anode film. Upon reaching the solution side of this layer, a region where the equilibrium concentration of cuprous ions is less, reaction (I) goes to the left, and metallic copper is precipitated as a very finely divided powder. Table I shows that, in the absence of chlorides, this powder formation is rather small, since most of the cuprous ions diffusing from the anode film merely serve to re-establish the cuprous ion concentration in the solution, which is constantly being depleted by oxidation and hydrolysis. It is interesting to note that, upon formation of metallic copper according to reaction (I), an equivalent amount of cupric ions is also formed, resulting in a steady increase of the cupric ion content of the solution as electrolysis proceeds. Similarly, the acidity will slowly decrease with time, owing to the oxidation of cuprous ions in the solution. Since the cuprous ions continuously leaving the anode film must be replaced to maintain the equilibrium value, reaction (V) must also occur concurrently with (IV), and it is seen at once that copper, even under ideal conditions, must dissolve anodically with at least slightly greater than 100 per cent efficiency.

If now the addition of chloride ions to the solution is considered, the free chloride migrating to the anode film will cause further precipitation of cuprous chloride. The amount of cuprous chloride formed in the film will be considerably larger than in the body of the solution and cuprous chloride will diffuse across the anode layer. Two possibilities must now be considered in turn. If the original addition of chloride to the solution was small, say up to about 50 mg/l, the concentration of Cu^+ ions in the solution will not be appreciably decreased and will soon be restored to the equilibrium value. It will be possible for the molecules of CuCl which have diffused away from the anode layer to dissociate back into chloride and cuprous ions according to equation (II), and the latter will, in turn, precipitate metallic copper since the equilibrium value for the cuprous ions is now exceeded. Powder formation in the presence of chlorides will therefore follow the overall reaction:

$$2CuCl \rightarrow Cu^{++} + 2Cl^- + Cu. \qquad (VII)$$

However, if large additions of chloride have been made to the solution, the concentration of free cuprous ions in the solution will be drastically reduced, its free chloride ion concentration will be correspondingly increased, and although the formation of cuprous chloride in the anode film will be higher, less and less of the CuCl diffusing across the anode layer will dissociate according to the above equation as the chloride content increases. Table I clearly shows that as the yield of copper powder decreases after passing through a maximum, that of cuprous chloride increases. Anode convection currents will at first wash away the undissociated salt, and may even carry it to the cathode, where its presence may be responsible for the deep vertical convection lines which have been observed. At still higher concentrations of chloride, the cuprous chloride forms a slowly growing film on the anode.

The effect of chloride ions on the anode processes does not seem to be altered in any way when bindarine is added to the system, but it is strikingly changed when gelatin and chloride are both present. Whereas a maximum powder formation amounting to about 2 per cent of the weight of the deposit in the coulometer was observed at 25°C in the presence of chloride alone, optimum concentrations of chloride and gelatin increased the powder formation to 39.5 per cent, indicating that the anode now dissolved largely in the cuprous form. This phenomenon can be explained in the light of the proposed mechanism if it is assumed that the effective concentration of cuprous chloride in the solution is radically decreased, allowing the dissociation of the salt formed in the anode film to proceed unhampered upon diffusion to the solution side of the anode layer. Formation of a complex between cuprous chloride and gelatin appears to be a reasonable possibility, as it has been shown to occur at least in basic media not only with gelatin but with other proteins as well (22–24). The large increase in powder formation can be explained by accelerated diffusion under the influence of a much larger effective concentration gradient.

The Cathode Processes

In the absence of chlorides or addition agent, the three following cathode reactions are possible:

$$Cu^{++} + 2e \rightarrow Cu, \qquad (VIII)$$

$$Cu^{+} + e \rightarrow Cu, \qquad (IX)$$

$$Cu^{++} + e \rightarrow Cu^{+}. \qquad (X)$$

Under steady state conditions in the cathode film, reaction (VIII) preponderates, since (IX) cannot occur until the potential requirements for the deposition of cuprous ions are met. If the cuprous ion concentration demanded by equation (I) were at all times maintained, reaction (VIII) would be the only one to occur, and two faradays of electricity would convert one gram ion of cupric ions to metallic copper. The efficiency of deposition in this case would be 100 per cent. In practice, however, depletion of the cuprous ions does occur, and to restore the equilibrium, reaction (X) must take place to some extent, resulting in less than 100 per cent efficiency of deposition. It can be predicted, therefore, that all conditions leading to depletion of the cuprous ions by favoring its oxidation and hydrolysis, such as dissolved oxygen, low acidity, high temperature, low apparent current density (or, alternatively, current densities near the critical value), will decrease the cathode efficiency. Ample experimental evidence has been presented to support these views. As an example of an extreme case, it is possible to electrolyze a strong, hot copper sulfate solution at low current density with no copper whatever depositing at the cathode, the whole of the current being used for the conversion of cupric to cuprous ions (25, 26).

The cathode behavior will not be greatly affected in the presence of small additions of chloride, since no appreciable depletion of the cuprous ions in the film occurs, and deposition will proceed normally except for the addition agent effect resulting from adsorption of CuCl, with a corresponding increase in weight of the deposits, as shown by the first part of curve A, Fig. 1, bottom. But when the chloride ion concentration is high, the cuprous ions concentration will be depleted to a much greater extent, and the

reduction of Cu^{++} to Cu^{+} [reaction (X)] will proceed to an increasing extent, resulting in decreased deposition efficiency. The second part of curve A, Fig. 1, bottom, occurring beyond a critical chloride ion concentration of between 50 and 75 mg/l, is really a composite curve, representing a combination of the increase in weight due to CuCl adsorption, and the decrease due to lowered deposition efficiency.

Addition of bindarine to an electrolyte containing chloride ions does not in any way alter the various effects on the cathode process observed in the presence of chloride alone. Cuprous chloride is still adsorbed by the deposit, and to very nearly the same extent. Gelatin, however, appears to prevent the adsorption of CuCl by the deposit, as shown by the analytical tests, and also by the first part of curve B, Fig. 1, bottom, which does not exhibit the regular increase due to adsorption in presence of chloride alone. However, the second part of this curve closely follows the behavior of curve A, indicating that the depletion of cuprous ions in the cathode film must again operate. These observations, of course, support the assumption previously made that the effective concentration of CuCl in the solution is considerably reduced by the formation of a gelatin-cuprous chloride complex.

In an effort to explain the depression observed in the polarization-chloride ion concentration curve (Fig. 3), further experiments were made at low halide concentrations in the presence of gelatin. Entirely new phenomena were encountered, discussion of which will be presented in a subsequent paper.

Acknowledgment

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Any discussion of this paper will appear in a Discussion Section, to be published in the December 1952 issue of the Journal.

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Concentration Polarization during Copper Deposition in a Convection-free System[1,2]

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ABSTRACT

By using a special type Haring cell, with the cathode in a horizontal position at the top, concentration polarization during deposition of copper was separated from other types of polarization. The slopes of the polarization-time curves during most of electrolysis were greater than could be explained by what is generally considered to be concentration polarization, and the discrepancy is explained on the basis of the ionic discharge theory of polarization.

Introduction

Only limited attention has been given in the past to the electrolytic deposition of copper under conditions such that convection currents, caused by density differences at the cathode, were eliminated. Sands (13) measured polarization in such a system, and found that the time at which the limiting current was reached, when a constant current was maintained, agreed with theoretical equations derived from the transport numbers of the ions in the electrolyte and the differential equation for the rate of diffusion of the ions that were reduced. Ibl and Trumpler (7) used a layer of barium sulfate on the cathode, placed horizontally at the bottom of the cell, to prevent convection currents, and found that the copper deposited with the limiting current (constant potential) was mainly in the powdered form. They (8) found fair agreement between their experimental results and those calculated from theoretical equations.

The equation relating concentration polarization, ΔE_c, with time, t, initial concentration, C_0, and constant apparent current density, i, derived for diffusion only is (12, 13)

$$\Delta E_c = -\frac{RT}{z\mathbf{F}} \ln (1 - 2i\sqrt{t}/z\mathbf{F}C_0\sqrt{\pi D}) \qquad (I)$$

where R, T, and $\mathbf{F}$ are, respectively, the gas constant, absolute temperature, and the faraday, and D and z are, respectively, the diffusion coefficient and the valence of the ions discharged. If the ions are brought to the cathode by diffusion and migration, the equation corresponding to (I) is (13):

$$\Delta E_c = -\frac{RT}{z\mathbf{F}} \ln (1 - 2it_- \sqrt{t}/z\mathbf{F}C_0\sqrt{\pi D}) \qquad (II)$$

where t_- is the sum of the transport numbers of all the ions in the diffusion layer except the copper ions.

When $\sqrt{t}$ becomes equal to $z\mathbf{F}C_0\sqrt{\pi D}/2i$ in equation (I) or $z\mathbf{F}C_0\sqrt{\pi D}/2it_-$ in equation (II), the logarithmic term in either equation approaches minus infinity and ΔE_c approaches infinity. This time, known as the transition time, is given the symbol τ and both of the above equations reduce to

$$\Delta E_c = -0.030 \log (1 - \sqrt{t}/\sqrt{\tau}) \text{ volts} \qquad (III)$$

when i is expressed in amp/cm^2, t in sec, C_0 in moles/ml, and D in cm^2/sec. It is further obvious from the above equations that for a given initial concentration

$$i\sqrt{\tau} = \text{constant}. \qquad (IV)$$

The experiments reported in this paper were made to determine the extent to which concentration polarization is responsible for the polarization measured during copper deposition in a convection-free system with a constant apparent current density.

Experimental

Equipment

The electrolytic cell had all the features of an ordinary Haring cell (6), except that the anode and cathode were placed at the bottom and top of the cell, respectively. A cross-sectional diagram of the cell, which was cylindrical in shape with internal diameter of 4.1 cm, is shown in Fig. 1. Three glass cylinders, H, were separated with rings of Lucite, and a ring of Lucite fitted over each end cylinder. This assembly, together with the $\frac{1}{16}$-inch sheet metal copper anode, A, which was attached to a Lucite block by a bolt welded to the anode and passing through a hole in the center of the block, was held together by five bolts, F. The two nonworking electrodes, B and C, were copper screens cut to fit inside the cell but with a few wires left protruding between and beyond two Lucite rings

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[2] Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, and the Division of Chemistry, Science Service, Department of Agriculture, Ottawa.

which served to hold the screens in place. The protruding wires acted as electrical connections with the electrodes. Before drawing the assembly together, the grooves in the Lucite rings into which the glass cylinders fitted, and the faces of the rings between which the wires of the screens passed, were softened with chloroform. The $\frac{1}{16}$-inch sheet metal copper cathode, D, was attached to a Lucite block in the same manner as the anode, and ground with emery on plate glass until the face was quite flat. The cathode and its Lucite block were attached to the remainder of the cell by five short bolts, E. The lower end of each of the five long bolts, F, fitted into a hole in a rubber stopper, I, so that the

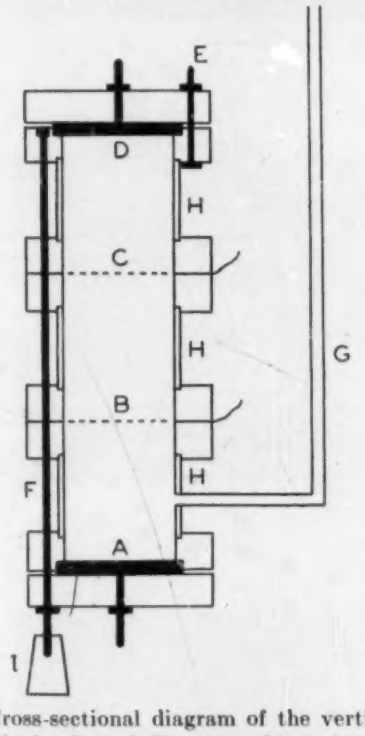

FIG. 1. Cross-sectional diagram of the vertical Haring cell. D—cathode, B and C—nonworking electrodes, A—anode, E—five short bolts, H—glass cylinders, F—five long bolts, I—five rubber stoppers, G—glass tube.

completely assembled cell rested in a vertical position on five rubber stoppers with the cathode at the top.

The external voltage for the cell was supplied by a 6-volt storage battery, and the electrode potentials were calculated from measurements made with a Leeds & Northrup Type K potentiometer.

Procedure

A solution of 125 grams of copper sulfate pentahydrate and 100 grams of concentrated sulfuric acid per liter in redistilled water will be referred to as the standard electrolyte. In a few experiments, which will be indicated when the results are presented, this solution was diluted tenfold.

Different initial cathode surfaces were obtained by polishing with No. 4/0 emery paper, or grinding with 120-mesh emery powder on glass under water, or rubbing with No. 2 emery cloth. The surfaces were cleaned with benzene after preparation. Surfaces were also prepared by electrodeposition of copper with and without simultaneous hydrogen evolution.

The cell was filled before the cathode was attached. After the cathode was bolted in place, all air bubbles were carefully removed through the side arm, G (Fig. 1), and the level of the solution in the side arm was brought to the level of the cathode. The cell was placed inside a constant temperature air bath on a flat piece of metal which rested on three wedges, and accurately leveled by adjusting the three wedges. The measurements of polarization were made in the same way as with an ordinary Haring cell (6).

RESULTS

Several experiments were made to determine the effect of apparent current density and temperature on the time required to reach the point of rapid increase in polarization. This was done to obtain an indication of the validity of the theoretical equations (given above) for the system used, and to determine the current density most convenient to use. These experiments were made with a cathode on which copper had been deposited without hydrogen evolution.

Table I shows that decreasing the apparent current density from $11.4 \cdot 10^{-3}$ to $4.55 \cdot 10^{-3}$ amp/cm^2 increased the time at which the rapid increase of polarization occurred from just over 5 minutes to approximately 34 minutes. The values for the constant in equation (IV) calculated from the experimental values at the different current densities were 26.7, 26.6, 26.7, 27.1, and 26.7 amp min$^{1/2}$ cm^{-2}, which shows the validity of this equation.

Table II shows the increase in time required to reach the rapid rise in polarization, at constant current, as the temperature was increased from 13.5° to 24.5°C. Since the diffusion coefficient of ions in solution becomes greater with increased temperature, these experimental results are in general agreement with the theoretical equations. The agreement between duplicate experiments, shown in the table, indicates the reproducibility that could be obtained.

Equations (I) and (II) imply that concentration polarization should not be affected by the previous treatment of the cathode. Experiments were therefore made with a number of different cathode surfaces at constant apparent current density and temperature. The results of these experiments, pre-

TABLE I. *Effect of apparent current density on the relation between time and polarization*

Standard electrolyte
Temperature: 25°C

Time min	Polarization—millivolts				
	amp/cm²·10³				
	11.4	7.58	6.06	5.68	4.55
0.25	90	68	—	—	—
0.50	93	73	49	48	37
1.0	103	77	—	53	43
1.5	—	—	60	—	—
2.0	118	87	63	59	47
3.0	135	93	—	—	—
4.0	161	99	74	68	54
5.5	600+	—	—	—	—
6.0		114	83	76	60
8.0		133	91	84	65
10.0		165	101	91	70
11.0		201	—	—	—
12.0		—	112	100	75
12.3		600+	—	—	—
14.0			125	109	80
16.0			143	120	85
18.0			183	135	91
19.5			600+	—	—
20.0				163	97
22.0				248	104
22.8				600+	—
24.0					112
26.0					121
28.0					132
30.0					151
32.0					189
34.0					311
34.5					600+

TABLE II. *Effect of temperature on the relation between time and polarization*

Standard electrolyte
Current: $6.0 \cdot 10^{-3}$ amp/cm²

Time min	Polarization—millivolts					
	13.5°C		20.0°C		24.5°C	
	1	2	1	2	1	2
0.25	—	—	—	—	—	76
0.50	—	—	98	—	—	—
1.0	116	115	—	101	97	90
2.0	119	118	103	105	94	93
4.0	128	129	110	113	102	100
6.0	140	140	118	120	110	109
8.0	156	155	128	129	119	118
10.0	181	178	140	139	130	128
12.0	216	215	156	155	139	140
14.0	600+	600+	185	179	154	156
16.0			263	228	180	184
17.0			600+	600+	—	—
18.0					246	265
19.0					600+	600+

sented in Fig. 2, show that, although the polarization values during most of the electrolysis varied greatly with the different initial surfaces, the time required to reach the rapid increase of polarization was the same in all cases. The broken line shows the theoretical polarization-time curve calculated from equation (III) with τ equal to the experimental value taken from the figure. The polarization values in all cases were considerably higher than the theoretical values calculated from equation (III) during most of the electrolysis.

With the surfaces prepared with emery, the polarization values in Fig. 2 showed a fairly sharp increase early in the electrolysis, after which they leveled off considerably until the final rapid increase occurred. The time of the first increase was the same (about 2 min) for the surfaces prepared with

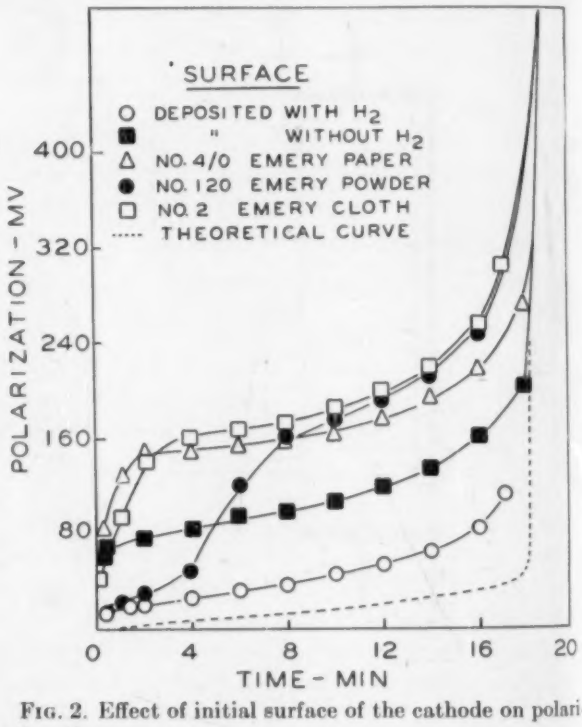

FIG. 2. Effect of initial surface of the cathode on polarization-time curves.

No. 4/0 emery paper and with No. 2 emery cloth, but for the surface prepared with 120-mesh emery powder this time was extended to about 4 minutes. Experiments with cathodes prepared with 120-mesh emery powder, at a reduced current density of $6.72 \cdot 10^{-4}$ amp/cm² and with tenfold dilution of the standard electrolyte, did not show this first break in the polarization-time curve, even though the total time of electrolysis, to the final rapid increase, was somewhat longer than in the previous experiment (Fig. 2). It is believed, therefore, that the increase at about 4 minutes in Fig. 2, with the higher current density, was due to change in the surface as a result of copper deposition (4), and independent of concentration changes in the electrolyte near the cathode.

In an effort to obtain further information about the extent to which polarization during the early part of electrolysis could be accounted for by concentration polarization, an oscilloscope (DuMont, at intervals during electrolysis, and photographs were taken of the instantaneous decay and build-up of polarization, as indicated by the oscilloscope trace. Measurements were also made with the

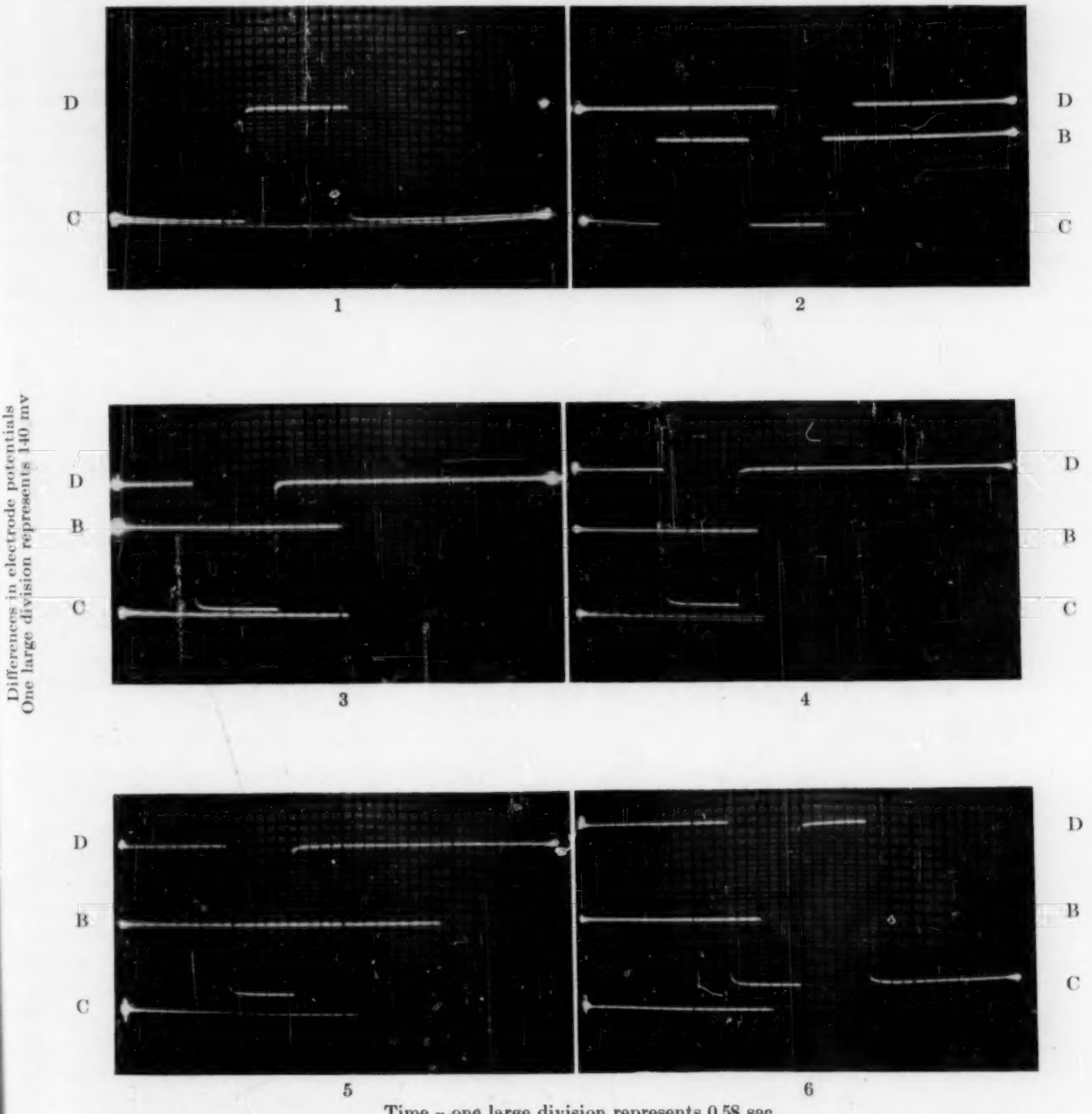

FIG. 3. Oscilloscope photographs of initial build-up and decay of polarization. The distance from line C to line D represents the potential difference between the nonworking electrode and the cathode while the distance from C to B represents the potential difference between the two nonworking electrodes (see Fig. 1). The distance from B to D represents total polarization, and residual polarization (circuit broken) is represented by the distance from C to the short line directly below the break in line D.

304–H) was connected to the potentiometer circuit through a two-way switch so that the two could be interchanged instantaneously. With this arrangement the oscilloscope was switched into the circuit potentiometer at the usual intervals. Six photographs, taken during one experiment, are shown in Fig. 3. Film 1 shows the initial build-up of polarization and the decay a fraction of a second later.

Film 2 resulted when the circuit was broken for a fraction of a second following one-half minute of electrolysis (the line for residual polarization is blurred but shows the general position), and films 3, 4, 5, and 6 were similarly produced after 5, 9, 13, and 16 minutes of electrolysis, respectively. The traces on the photographs are lettered to correspond to those of the cell (see Fig. 1), that is, the distance from D to C represents the voltage from D to C in the cell and the distance from B to C represents the voltage between the two nonworking electrodes B and C. The distance from C to the short line directly below the break in D shows the residual polarization after instantaneous decay, while the distance from B to D is the total polarization of the

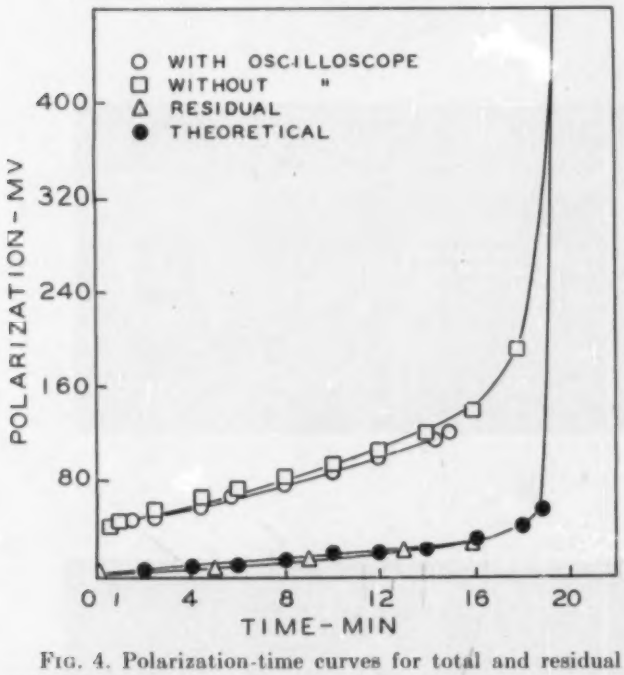

FIG. 4. Polarization-time curves for total and residual polarization.

cathode. Since the sweep time of oscilloscope was 2.3 sec, it is obvious from the photographs that a large part of the polarization build-up and decay was almost instantaneous.

Fig. 4 shows the residual polarization from Fig. 3 and the total polarization, measured with the potentiometer, for the same experiment, plotted against time. The corresponding curve for an experiment exactly the same but in the absence of momentary breaks in the current, and the theoretical concentration curve calculated from Equation (III) with τ equal to 19.5 minutes, are included in the figure for comparison. From this figure it is apparent that the residual polarization corresponds to the theoretical concentration polarization from zero time to 16 minutes but that the slopes of the total polarization-time curves are greater than for concentration polarization.

The difference between the slope of the experimentally determined polarization-time curve (total polarization) and the slope for theoretical concentration polarization is illustrated clearly in Fig. 5, where the experimental slope is the average of 12 experiments with a deposited surface. The cathode was in contact with the electrolyte for periods of time varying from 4 minutes to 3 hours, and in some of the experiments oxygen was removed from the electrolyte before electrolysis while in others it was not. In these experiments the maximum deviation from the average slope shown in Fig. 5 was about 5 mv.

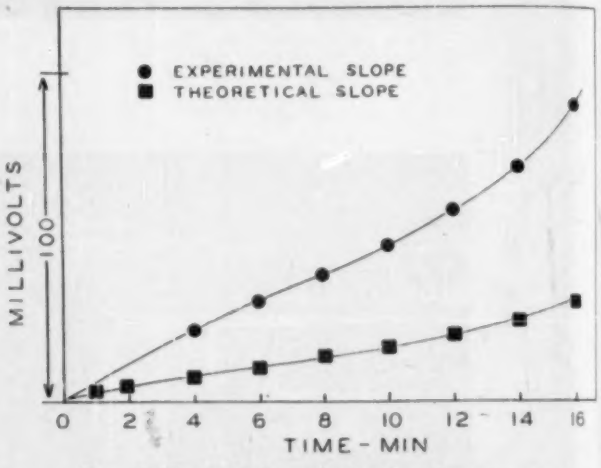

FIG. 5. Slope of the polarization-time curves

DISCUSSION AND CONCLUSIONS

Since the hydrogen ion has a much greater mobility than the copper ion, and the ratio of hydrogen to copper ion in the diffusion layer increases with approach to the cathode, equation (I) should be superior to equation (II) for electrolysis with the standard electrolyte. The diffusion coefficients, calculated from equation (I), for apparent current densities of $11.4 \cdot 10^{-3}$, $7.58 \cdot 10^{-3}$, $6.06 \cdot 10^{-3}$, $5.66 \cdot 10^{-3}$, and $4.55 \cdot 10^{-3}$ amp/cm^2 (Table I) were, respectively, $5.84 \cdot 10^{-6}$, $5.75 \cdot 10^{-6}$, $5.85 \cdot 10^{-6}$, $5.99 \cdot 10^{-6}$, and $5.83 \cdot 10^{-6}$ cm^2/sec at 25°C; and for temperatures of 13.5°, 20.0°, and 24.5°C with an apparent current density of $6.0 \cdot 10^{-3}$ amp/cm^2 (Table II) they were, respectively, $4.12 \cdot 10^{-6}$, $5.00 \cdot 10^{-6}$, and $5.59 \cdot 10^{-6}$ cm^2/sec. The satisfactory agreement between these values of the diffusion coefficient at the different temperatures and those reported in the literature (3, 10) provides justification for using equation (III) to calculate the fraction of the total polarization caused by concentration polarization.

It appears that a satisfactory explanation for the difference between the slopes of the experimental

and theoretical curves in Fig. 5 can be given on the basis that ionic discharge is a slow process. According to this theory, the equation relating current density i, with polarization ΔE, and initial concentration C_0, is (5):

$$i = I_0 \left(e^{\alpha z \mathbf{F} \Delta E/RT} - e^{-(1-\alpha) z \mathbf{F} \Delta E/RT}\right) \qquad \text{(V)}$$

where I_0 is the current flowing in each direction at equilibrium and α is a constant with a value between zero and unity. Concentrations are used here instead of activities since only a semiquantitative treatment is attempted. Equation (V) does not show the effect of concentration changes at the electrode on polarization but this can be remedied by replacing C_0 with C_e, the concentration at the electrode when there is a net flow of current, in its derivation. When this is done equation (V) becomes

$$i = I_0 \left(\frac{C_e}{C_0} e^{\alpha z \mathbf{F} \Delta E/RT} - e^{-(1-\alpha) z \mathbf{F} \Delta E/RT}\right). \qquad \text{(VI)}$$

One logarithmic form of equation (VI) is

$$\Delta E = \frac{RT}{z\mathbf{F}} \ln \frac{C_0}{C_e} + \frac{RT}{z\mathbf{F}} \ln \left(1 + \frac{i}{I_0} e^{(1-\alpha) z \mathbf{F} \Delta E/RT}\right). \qquad \text{(VII)}$$

The first term on the right hand side of equation (VII) is the usual expression for concentration polarization, on which equations (I) and (II) are based, while the second represents activation polarization (1, 11). Another logarithmic form of equation (VI) is

$$\Delta E = \frac{RT}{\alpha z \mathbf{F}} \ln \frac{C_0}{C_e} + \frac{RT}{\alpha z \mathbf{F}} \ln \left(\frac{i}{I_0} + e^{-(1-\alpha) z \mathbf{F} \Delta E/RT}\right) \qquad \text{(VIII)}$$

The first term on the right hand side of equation (VIII) is the same as the usual expression for concentration polarization except for α in the denominator of the coefficient of $\ln C_0/C_e$. Since α is less than unity, equation (VIII) shows that the effect of at least part of activation polarization is to increase the slope of the polarization-time curve over that calculated for concentration polarization alone. This observation is in general agreement with the results shown in Fig. 5. It should be noted that the inclusion of α in the expression for concentration polarization has no effect on the transition time [see equation (III)]. The part of activation polarization represented in the second term on the right hand side of equation (VIII) should be practically constant, providing the constant current i is considerably larger than I_0. An equation similar in most respects to (VI) can be derived from the quantum statistical treatment of polarization (2, 9).

There was apparently some correlation between the initial polarization values shown in Fig. 2 and the true surface area of the cathode. For instance, the polarization values after ½ minute of electrolysis were about the same, 63 and 64 mv, respectively, for the surface deposited without simultaneous evolution of hydrogen and that prepared with No. 2 emery cloth; for the surface prepared with 120-mesh emery powder it was only 20 mv. The true surface areas reported by Wiebe, *et al.*, (14) varied from 30 to 61 times planar for the former two kinds of surfaces and from 163 to 287 times planar for the latter.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1952 issue of the JOURNAL.

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The Effects of Halides on Copper Deposition in the Presence of Gelatin[1, 2]

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ABSTRACT

In the electrodeposition of copper from acid copper sulfate electrolytes, the steady state cathode polarization was found to be independent of initial surface in the presence of 25 mg/l of gelatin and higher. Chloride, bromide, and iodide ions in presence of gelatin yielded polarization-halide concentration curves with minima, while fluoride ions had no effect. These minima were independent of acid concentration and shifted to higher halide concentrations and higher polarization with increase in current density or gelatin concentration. An increase in temperature shifted the minimum of the polarization-chloride concentration curve to lower values. The general trends in polarization with changes in halide concentration were shown to be independent of the method of measurement and the geometry of the cells. Excess weights (i.e., weight of deposit in excess of that obtained in a coulometer in series with pure copper sulfate electrolyte) increased to constant values with increasing chloride concentration. The gelatin content of the deposits was constant over a large range of chloride concentrations, while the chloride content passed through a maximum. The various observations have been explained on the basis of formation of crystal imperfections on the cathode by the halides, in conjunction with addition agent effects of gelatin and cuprous halide.

Introduction

Some effects observed when chloride and gelatin were used together during electrodeposition of copper from acid copper sulfate electrolytes have been described in a previous paper from this laboratory (4). The chloride concentrations used were in excess of 10 mg/l. When the study was extended to lower concentrations of chloride, the results outlined in the present paper were obtained.

Experimental and Results

Cathode Polarization

Polarization measurements were generally made in a Haring cell (8) which consisted of 1-cm thick Lucite sheets assembled to form a rectangular box of inner dimensions 15 x 2.5 x 9 cm. The cathode and anode were copper strips 10 x 2.5 cm sealed with paraffin wax into recesses in the Lucite ends of the cell to give a flush mounting. The intermediate copper gauze electrodes were fitted into grooves in the side walls. The amount of electrolyte used was always 150 ml, which covered 10 cm^2 of electrode area. The cell was immersed in a thermostat to provide temperature control. Potential and current measurements were made with a Queen potentiometer, model E-3040, and a Weston milliammeter, model 45, respectively.

Electrolytes were made with doubly-distilled water, and contained 125 g/l of copper sulfate pentahydrate. The acid content was usually 100 g sulfuric acid per liter. "Eimer and Amend granular" gelatin from a single stock was used throughout. Halide ion was introduced as an aqueous solution of the sodium halide.

As in previous studies (5, 6), it was found that the cathode polarization attained a steady state value after one hour of deposition, such that further change in the polarization did not exceed 0.2 mv/min. For given conditions of electrolysis, the steady state values showed a maximum deviation of ±7 per cent. The cathode polarizations reported for the Haring cell are all steady state values.

Effect of Initial Surface

At moderate current densities and in the absence of addition agents, the initial surface condition of the cathode may affect the structure of the deposit (9) and the polarization. The significance of the polarization data may therefore be obscured by the effect of initial surface unless reproducible initial surfaces are used.

Experiments were made with gelatin concentrations of 10, 25, and 75 mg/l, at current densities of 1.0, 2.0, and 3.0 amp/dm^2, to determine the effect of initial surface on the polarization in the presence

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[2] Contribution from the Physical Chemistry Laboratory, McGill University, with financial assistance from the National Research Council of Canada.

[3] Holder of a National Research Council of Canada Fellowship.

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of addition agent. Four different surfaces were used, namely polished, etched, crystalline, and fine-grained. The latter two were obtained by deposition on etched cathodes from acid copper sulfate electrolyte, containing no addition agent, at 1.0 and 3.0 amp/dm², respectively.

With gelatin concentrations of 25 mg/l and higher, no effect of initial surface on cathode polarization was observed. Similar results were obtained when chloride was present in electrolytes containing gelatin.

Polarization-Halide Concentration Relations

The effect of fluoride ion on copper deposition in the presence of 25 mg/liter of gelatin and at a current density of 2 amp/dm² was investigated at concentrations ranging from 0 to 6 milliequivalents (M.E.) per liter. Neither the polarization nor the structure was affected by the addition of fluoride ions.

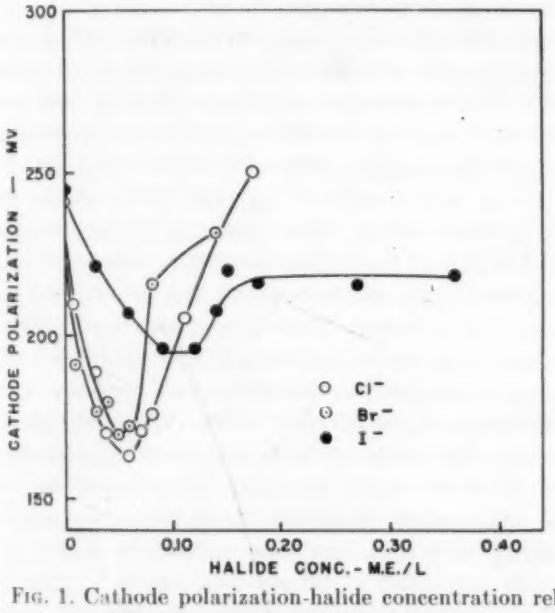

FIG. 1. Cathode polarization-halide concentration relations in the deposition of copper from acid copper sulfate solutions containing 25 mg/l gelatin. Current density: 2 amp/dm² (M.E. = milliequivalent).

Successive increases of chloride, bromide, or iodide concentration in the presence of gelatin first decreased the polarization and then increased it, thereby yielding polarization-halide concentration curves with minima (Fig. 1). It is evident that chloride and bromide affected polarization to about the same extent. Iodide was less effective, however, since the minimum of the polarization iodide concentration curve occurred at a greater concentration and at a greater polarization than with the other two ions. In general, the polarization-halide concentration curves were found to be altered by changes in current density, gelatin concentration, and temperature but not by changes in acid concentration. Thus, the minima for chloride and bromide shifted to higher halide concentrations and higher polarizations with increased gelatin concentration or current density (Fig. 2). With iodide, a change in current density from 2 to 3 amp/dm² shifted the minimum to a higher polarization but not to higher iodide concentration. At 40.0°C, the minimum of the polarization-chloride concentration curve shifted to a lower polarization and a lower concentration (Fig. 3), but at this temperature addition of iodide produced very little effect on polarization.

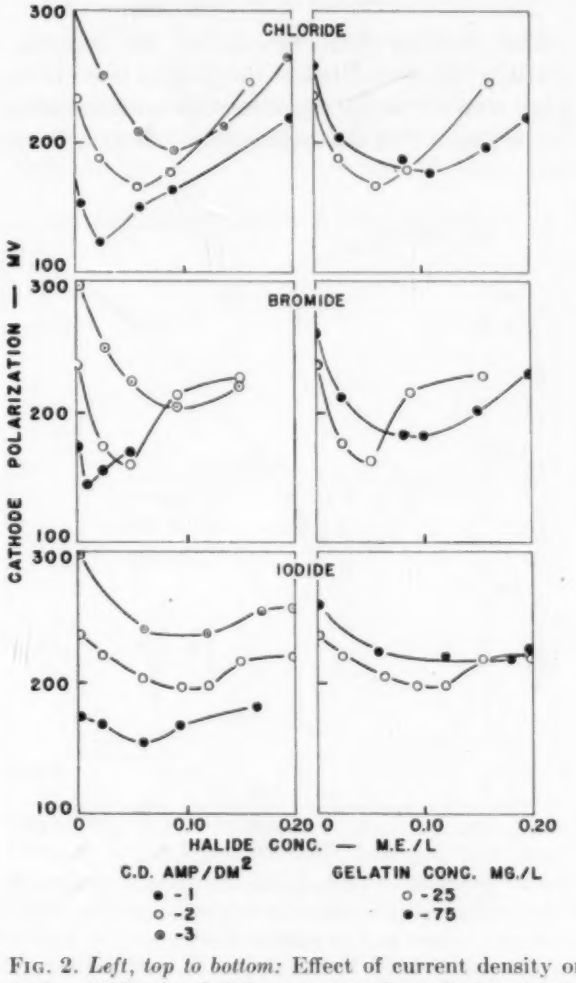

FIG. 2. *Left, top to bottom:* Effect of current density on cathode polarization-halide concentration relations in the deposition of copper from acid copper sulfate solutions containing 25 mg/l gelatin. *Right, top to bottom:* Effect of gelatin concentration on cathode polarization-halide concentration relations in the deposition of copper from acid copper sulfate solutions at a current density of 2 amp/dm² (M.E. = milliequivalent).

The form of the polarization-halide concentration curves remained unaltered when measurements were made with a probe in a cell in which the anode was surrounded by a parchment membrane and the inter-

mediate electrodes were removed. Hence, the observed minima were not attributable to insoluble material originating at the anode. Similar measurements in cells with concentric cylindrical electrodes also gave a polarization-chloride concentration curve with a minimum. The type of curve obtained was therefore not peculiar to the geometry of the Haring cell.

Structure of the Deposits

The physical characteristics of the deposits invariably depended upon the halide concentration used, relative to the concentration corresponding to the minimum in the polarization-halide concentration curve.

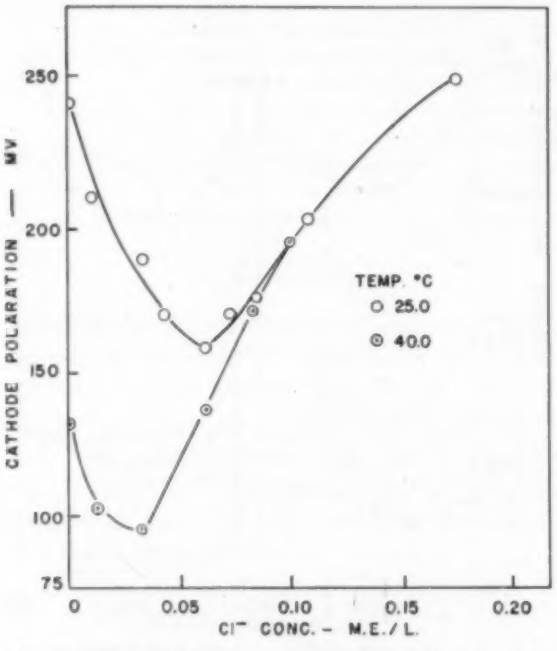

FIG. 3. Effect of temperature on cathode polarization-halide concentration relations in the deposition of copper from acid copper sulfate solutions containing 25 mg/l gelatin. Current density: 2 amp/dm² (M.E. = milliequivalent).

With increases in concentration of chloride, the deposits became increasingly brighter until the concentration corresponding to the minimum polarization was reached. At higher concentrations, the deposits became progressively more striated. The striations were visible as early as two minutes after deposition was begun, and consisted of smooth vertical streaks separated by apparently passive areas where little or no deposition seemed to occur. At high chloride concentrations, such that the polarization was the same magnitude as in the absence of chloride, the deposits contained a large number of nodules. At still higher chloride concentrations, uniform but dull deposits, with roughness at exposed edges, were obtained.

With increase in concentration of bromide, the appearance of the deposit passed through stages essentially similar to those observed with chloride, but the deposit had a reddish tint at all concentrations.

Increase in concentration of iodide beyond the minimum gave rise to randomly scattered, dark pock marks on the surface. These increased in number as the iodide concentration was increased. At all concentrations of iodide, the deposits had a dark hue.

Excess Weights and Analyses of Deposits

Excess weights, and gelatin, chloride, and sulfate contents, were determined for deposits obtained from electrolytes containing 25 mg/l of gelatin and various amounts of chloride.

Several cells were connected in series, each of which consisted of a 1-l beaker containing 800 ml of electrolyte. The anode was a copper cylinder that lined the inner wall of the beaker, and the cathode was a thin-walled copper tube of 1.8-cm diameter. The cathode was completely covered with paraffin wax on its inner surface, while the outer surface was covered with wax for a distance of 0.3 cm from the bottom and again at the top, leaving an exposed portion of 5-cm length. The exposed area was etched in 40 per cent nitric acid, rinsed with distilled water, dried overnight in a desiccator, and weighed before use. A thin layer of oxide which formed during this preparation of the cathode was found to contribute no significant change in weight. After deposition from the appropriate electrolyte for 5 hours at a current density of 2 amp/dm², the cathode was removed, rinsed and dried as before, and weighed again. By reference to the weight of deposit obtained in one of the cells which contained no gelatin or chloride, the excess weight of a deposit was immediately obtained. After the excess weight had been determined, the deposits were carefully turned off on a lathe for further analyses.

The gelatin content of each deposit was determined by combustion of a weighed portion of the fine lathe turnings at 900°C in a stream of oxygen (170 ml/min). The carbon dioxide was absorbed in 20 ml of 0.008*N* barium hydroxide solution containing 2.5 mg/l of gelatin and 5 ml/l of isopropyl alcohol, as foaming agents. An absorber containing silver permanganate and zinc oxide was placed in the combustion train to remove chlorine, hydrogen chloride, and oxides of sulfur that might have been evolved during the combustion (3). After 30-min combustion (shown empirically to be sufficient for complete combustion), the excess barium hydroxide was titrated. The amount of carbon dioxide so determined was expressed in terms of an equivalent amount of gela-

tin by reference to a calibration curve determined empirically by the same combustion procedure.

For chloride analysis, 2 grams of the lathe turnings were dissolved in 25 ml of 22.5 per cent nitric acid, the resulting solution diluted to 50 ml, and the reversible potential determined for the cell

$$\text{Ag, AgCl} \left| \begin{matrix} \text{Cl}^-, \text{Cu}(\text{NO}_3)_2, \\ \text{HNO}_3 \end{matrix} \right| \text{sat'd. calomel.}$$

The silver-silver chloride electrode was prepared by the method of Yao (10), and the saturated calomel electrode was of the type used for potentiometric titrations, with a pinhole for liquid contact. The cell was painted black and kept at 25°C during measurements. By maintaining the copper and nitric acid concentrations constant, the reversible potentials were found to be dependent on the chloride concentration, and to be essentially independent of the presence of gelatin and sulfate. Analyses were based on a calibration curve obtained empirically. (A similar method for chloride analysis, using a glass electrode instead of the saturated calomel electrode, has been used by others (1).)

Sulfate analyses were made by standard gravimetric procedure, after dissolving a portion of the deposit in nitric acid and converting the nitrate into chloride.

It is of interest, perhaps, to note that deposits, obtained from electrolytes containing gelatin, dissolved in nitric acid more slowly than those obtained from gelatin-free electrolyte, and that the rate of solution was further progressively reduced as the chloride content of the electrolyte was increased.

The per cent excess weights, and the gelatin and chloride contents of the deposits, are plotted in Fig. 4 as functions of the chloride concentrations of the electrolytes. It will be noted that a slow increase in excess weight with chloride concentration, up to and slightly beyond the chloride concentration corresponding to the minimum in the polarization-chloride concentration curve, was succeeded by a rapid increase with further increase in chloride content of the electrolyte. The gelatin content of the deposit remained essentially constant over most of the range of chloride concentrations in the electrolyte. On the other hand, the chloride content of the deposit showed a maximum at approximately the chloride concentration in the electrolyte corresponding to the minimum in the polarization-chloride concentration curve. Analytical values for the sulfate content of the deposit are not plotted since these were obtained only for a few samples. They were sufficient to demonstrate, however, that the combined gelatin, chloride, and sulfate contents of the deposits were quite inadequate to account for the excess weights, particularly with the higher chloride concentration in the electrolyte. Under the latter conditions, moreover, no sulfate could be detected in the deposit.

Discussion

In seeking an explanation of the observed trends in cathode polarization with variation of halide concentration in the electrolyte, it should be recalled that geometry of the electrolytic cell, and anode processes resulting in the formation of insoluble materials, apparently play no part. Moreover, at the relatively low halide concentrations used, it seems unlikely that cuprous halide should form in the electrode films and be adsorbed on the cathode in the manner suggested previously for higher chloride concentrations (4).

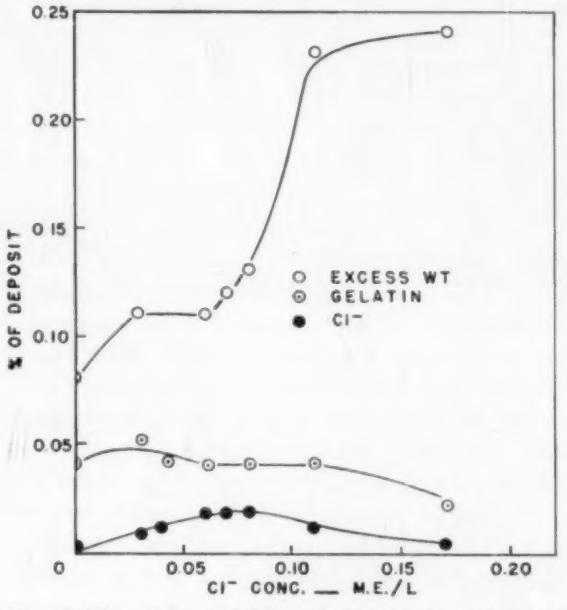

Fig. 4. The excess weight, and the gelatin and chloride contents of copper deposited from acid copper sulfate solutions containing 25 mg/l gelatin, and varying amounts of chloride. Current density: 2 amp/dm² (M.E. = milliequivalent).

The minima in the polarization-halide concentration curves suggest a balance between two processes that operate simultaneously to alter the polarization when both gelatin and halide are present in the electrolyte. Since interaction between gelatin and halide seems quite unlikely in the presence of the large excess of sulfate in the electrolyte, one of the processes may reasonably be associated with the gelatin, and the other quite independently with the halide.

The increase in polarization observed in the presence of gelatin alone has been interpreted as a consequence of the increased current density, which results when the active area of the cathode is reduced by adsorption of gelatin on active centers of the cathode surface (7). Over a considerable range

of chloride concentration the adsorption of gelatin on the cathode appears to be relatively unaffected (Fig. 4). The independent action of the halide ions mentioned previously might therefore be assumed to involve the less active parts of the cathode surface. If the increase in polarization observed with gelatin alone is associated with a decrease of active cathode area, then by analogy the decrease in polarization accompanying small additions of halide may be attributed to an increase in active area.

In summary, then, the halide is responsible for independent action on relatively inactive portions of the cathode surface, with a resultant increase in active area. It is suggested that this increase is brought about by attack of halide at crystal faces on the cathode surface with the production of lattice imperfections, a process which might be expected to increase the number of active centers available for deposition. Such attack should occur, in view of the observed increase in chloride concentration in the cathode film (11) and the tendency for cuprous halide formation. Analogous behavior on a macro scale can be found in the corrosion (oxidation) of copper by halide ions, where the effectiveness of the halide ion was found to be greater, the more insoluble the cuprous halide formed (2). It is interesting, moreover, that fluoride did not corrode copper, while chloride, bromide, and iodide did. This observation has its parallel in the present study in the failure of fluoride, unlike the other halides, to affect the polarization.

With increasing halide concentration there should be a greater tendency for cuprous halide to form or be adsorbed on the cathode surface and exert an addition agent effect similar to that of gelatin. If this effect eventually becomes predominant over the tendency for halide to cause an increase in active area of the cathode, the polarization should pass through a minimum as observed. The maximum chloride content of the deposit does, in fact, correspond approximately to the minimum of the polarization-chloride concentration (in electrolyte) curve (Fig. 4).

From the preceding discussion, it might be expected that an increase in gelatin concentration should render the cathode less susceptible to halide attack and therefore shift the minimum in the polarization-halide concentration curves toward higher values of both polarization and halide concentration. This expectation is realized experimentally (Fig. 2). The similar shift with increase in current density, at given gelatin concentration, may be attributed to the greater tendency for halide ion to migrate away from the cathode.

The somewhat different behavior of iodide, as compared with chloride and bromide, might be due simply to occurrence of the well-known reaction

$$2CuI_2 \rightarrow 2CuI + I_2.$$

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Any discussion of this paper will appear in a Discussion Section, to be published in the December 1952 issue of the JOURNAL.

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